Occupational Health Guideline for Petroleum Distillates (Naphtha)

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: $C_6H_{14}-C_7H_{16}-C_{8H1}$
- Synonyms: Petroleum naphtha; aliphatic petroleum naphtha; petroleum ether (95 to 115 C); naphtha, petroleum
- Appearance and odor: Colorless liquid with an odor like gasoline and kerosene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for petroleum distillates is 500 parts of petroleum distillates per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2000 milligrams of petroleum distillates per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit be reduced to 350 mg/m³ averaged over a work shift of up to 10 hours per day, 40 hours per week.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Petroleum distillates can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to petroleum distillates may cause dizziness, drowsiness, headache, and nausea. They may also cause irritation of the eyes, throat, and skin.

2. Long-term Exposure: Prolonged overexposure may cause drying and cracking 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 petroleum distillates.

- **Recommended medical surveillance**

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

—Skin disease: Petroleum distillates are skin 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.

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

—Liver disease: Although petroleum distillates are not known as liver toxins 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 petroleum distillates 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.

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

- **Summary of toxicology**

The vapors of petroleum distillates are mild narcotics and mucous membrane irritants. There have been few toxicologic studies, either on animals or man. While 4000 to 7000 ppm are tolerated for 1 hour by human subjects, symptoms of narcosis, such as dizziness and drowsiness, occur at those concentrations. Continuing

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 may produce signs of inebriation, followed by headache or nausea. Exposure at 10,000 to 20,000 ppm is regarded as immediately hazardous to life. The higher boiling fractions may produce irritation of the eyes, nose, and throat in addition to symptoms of mild narcosis. The liquid is a defatting agent, and repeated or prolonged skin contact results in drying and cracking of the skin. No chronic systemic effects have been reported from widespread industrial use. If benzene is present in the distillate, however, the hazard of both acute and chronic poisoning is increased; the presence of elevated phenol in the urine is indicative of benzene exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 100 (approximately)
2. Boiling point (760 mm Hg): 30 to 127 C (86 to 260 F)
3. Specific gravity (water = 1): 0.74
4. Vapor density (air = 1 at boiling point of petroleum distillates): 3.4 (approximately)
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 40 mm Hg (approximately)
7. Solubility in water, g/100 g water at 20 C (68 F): 0.04 (approximately)
8. Evaporation rate (butyl acetate = 1): 10 (approximately)

- **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 petroleum distillates.
4. Special precautions: Petroleum distillates will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −40 to 20 C (−40 to 68 F) (closed cup)
2. Autoignition temperature: 232 to 260 C (450 to 500 F)
3. Flammable limits in air, % by volume: Lower: 1; Upper: 6
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: The odor thresholds of the main constituents of petroleum naphtha (i. e., heptane, octane, pentane, etc.) are below the individual permissible exposure limits.
2. Eye Irritation Level: According to Gafafer, the naphthas irritate the conjunctiva. The American Petroleum Institute states that irritation of the conjunctiva may occur "when the eyes are exposed to high vapor concentrations (of petroleum naphtha) in air. The irritation is mild and transitory." No quantitative information is available concerning the threshold of eye irritation, however.
3. Evaluation of Warning Properties: Since the odor of each of the main constituents of petroleum naphtha is detectable at concentrations below the respective permissible exposure limits, petroleum 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 petroleum distillates 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 petroleum distillates may be used. An analytical method for petroleum distillates 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 petroleum distillates.

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

• Any clothing which becomes wet with liquid petroleum distillates should be removed immediately and not reworn until the petroleum distillates are removed from the clothing.

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

SANITATION

• Skin that becomes wet with liquid petroleum distillates should be promptly washed or showered with soap or mild detergent and water to remove any petroleum distillates.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during degreasing operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as solvents in rubber industry during manufacture of waterproof cloth, shoe adhesives, and rubber tires	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as extractants; use in preparation of paint, varnish, and lacquer as solvents, diluents, or thinners; use as solvents in pesticides	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during dry 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 petroleum distillates 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 these chemicals.

• **Skin Exposure**

If petroleum distillates get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If petroleum distillates 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 petroleum distillates, 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 petroleum distillates have 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 petroleum distillates are 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. Petroleum distillates should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Petroleum distillates may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PETROLEUM DISTILLATES (NAPHTHA)

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 Health Guideline for Phenol

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_5OH
- Synonyms: Carbolic acid; monohydroxybenzene
- Appearance and odor: Colorless to pink solid or thick liquid with a characteristic, sweet, tarry odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phenol is 5 parts of phenol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 19 milligrams of phenol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 20 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 60 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Phenol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phenol 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: Phenol has a marked corrosive effect on any tissue. When it comes in contact with the eyes, it may cause severe damage and blindness. On contact with the skin, it does not cause pain but causes a whitening of the exposed area. If the chemical is not removed promptly, it may cause a severe burn or systemic poisoning. Systemic effects may occur from any route of exposure, especially after skin contact.

2. Long-term Exposure: Repeated or prolonged exposure to phenol may cause chronic phenol poisoning. The symptoms of chronic poisoning include vomiting, difficulty in swallowing, diarrhea, lack of appetite, headache, fainting, dizziness, dark urine, mental disturbances, and possibly a skin rash. Liver damage and discoloration of the skin 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 phenol.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phenol 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 or abnormalities of the skin, respiratory tract, liver, or kidneys would be expected to be at increased risk from exposure. Examination of the liver, kidneys, and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Darkening of the urine has occurred in persons exposed to phenol after accidental ingestion or skin contact. A urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Urinary phenol is useful if good individual background levels are available.

—Liver function tests: Since liver damage has been observed in humans exposed to phenol, a profile of liver function should be performed by using a medically acceptable array of biochemical tests.

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.

• **Summary of toxicology**

Phenol in the vapor form or in solution is an irritant to the eyes, mucous membranes, and skin; systemic absorption causes central nervous system effects as well as liver and kidney damage. Sudden collapse is characteristic of gross overexposure. In animals, prolonged inhalation of the vapor at 30 to 60 ppm induced respiratory difficulty, lung damage, and paralysis. Systemic absorption by animals caused muscle twitching and severe convulsions. There are no reports of human fatalities from inhalation of the vapor, although one case of severe poisoning has been reported. Ingestion of lethal amounts (as little as 1 g) cause severe burns of the mouth and throat, marked abdominal pain, cyanosis, muscular weakness, collapse, coma, and death; tremors, convulsions, or muscle twitching were occasionally observed but were not severe. A laboratory technician repeatedly exposed to unknown vapor concentrations and liquid spilled on the skin developed anorexia, weight loss, weakness, muscle aches and pain, and dark urine; during several months of nonexposure there was gradual improvement in his condition, but after brief reexposure he suffered an immediate worsening of symptoms with prompt darkening of the urine and tender enlargement of the liver. Brief intermittent industrial exposures to vapor concentrations of 48 ppm of phenol (accompanied by 8 ppm of formaldehyde) caused marked irritation of eyes, nose, and throat. Concentrated phenol solutions are severely irritating to the human eye and cause conjunctival swelling; the cornea becomes white and hypesthetic; loss of vision has occurred in some cases. Solutions of phenol have a marked corrosive action on any tissue on contact; on skin, there is local anesthesia and a white discoloration, and the area may subsequently become gangrenous; severe dermatitis will result from contact with dilute solutions, and prolonged exposure may result in ochronosis. In workers making phenol-formaldehyde plastic, the urinary level of total phenol, free plus conjugated, was proportional to the air concentration of phenol up to 12.5 mg/m^3 of workroom air. Mice were treated twice weekly for 72 weeks by application of 1 drop of a 10% solution of phenol in benzene to the shaved dorsal skin; after 52 weeks of treatment there were papillomas in 5 of 14 mice, and 1 fibrosarcoma appeared at 58 weeks.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 94.11
2. Boiling point (760 mm Hg): 182 C (359 F)
3. Specific gravity (water = 1): 107 (solid); 1.05 (liquid)
4. Vapor density (air = 1 at boiling point of phenol): 3.24
5. Melting point: 41 C (106 F)
6. Vapor pressure at 20 C (68 F): 0.36 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 8.4
8. Evaporation rate (butyl acetate = 1): Less than 0.01

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers (especially calcium hypochlorite) may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving phenol.
4. Special precautions: Liquid phenol will attack some forms of plastics, rubber, and coatings. Hot liquid phenol will attack aluminum, magnesium, lead, and zinc metals.

• **Flammability**

1. Flash point: 79 C (174 F) (closed cup)
2. Autoignition temperature: 715 C (1319 F)
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.6
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

• **Warning properties**

1. Odor Threshold: Summer reports that the odor threshold of phenol is 3 ppm; the Manufacturing Chemists Association reports 0.3 ppm; Thienes and Haley report 5 ppm.
2. Irritation Levels: The *Documentation of TLV's* reports that intermittent exposures to 48 ppm phenol have been observed to produce eye, nose, and throat irritation. Formaldehyde was also present in this atmosphere at a concentration of 8 ppm. The Respirator Review Committee considers the source of the eye irritation to be the 8 ppm formaldehyde rather than the phenol.
3. Evaluation of Warning Properties: Since the odor threshold of phenol is at or below the permissible exposure limit, phenol 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 phenol. 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 phenol in a bubbler containing sodium hydroxide, followed by treatment 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 phenol may be used. An analytical method for phenol 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 solid or liquid phenol or liquids containing phenol.

• If employees' clothing has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing which has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phenol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phenol, the person performing the operation should be informed of phenol's hazardous properties.

• Where there is any possibility of exposure of an employee's body to solid or liquid phenol or liquids containing phenol, 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 phenol should be removed immediately and not reworn until the phenol 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 phenol or liquids containing phenol contacting the eyes.

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

SANITATION

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

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

• Eating and smoking should not be permitted in areas where solid or liquid phenol or liquids containing phenol are handled, processed, or stored.

• Employees who handle solid or liquid phenol or liquids containing phenol 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 phenol may occur and control methods which may be effective in each case:

Operation	Controls
Application and curing of bonding resin in plywood manufacture; application and curing of molding resins in manufacture of molded articles, such as	Process enclosure; local exhaust ventilation; personal protective equipment

electrical appliances, automotive parts, foundry sand molds, and utensil handles; manufacture of friction materials, bonded abrasives, coated abrasives, wood particle board, and insulation materials	
Use in industrial coatings in drum and can linings, milk and beer-processing equipment, water tanks and air-conditioning equipment, decorative laminates, and textile coatings	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of thermosetting phenolic resins, epoxy, polycarbonate, phenoxy, and polysulfone; synthesis of aprolactam for use in nylon 6 fibers, plastics, and films	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of agricultural chemicals and intermediates; synthesis of pharmaceuticals, rubber and plastic plasticizers, antioxidants, curing agents, and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of stabilizers and preservatives for dyes, perfumes, and fungicides	Process enclosure; local exhaust ventilation; personal protective equipment
Use during solvent refining of lubrication oil and wax; use in synthesis of additives for gasoline and lubricating fluids and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of intermediates in polyester production; production of corrosion-resistant polyester and polyester polyols; use in synthesis of dye intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of surface-active agents and detergent intermediates; in synthesis of explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of disinfectant agents and products for industrial and household use	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of synthetic cresols and xylenols	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 solid or liquid phenol or liquids containing phenol 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 phenol or liquids containing phenol get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid phenol or liquids containing phenol 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 phenol, 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 phenol or liquids containing phenol 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 phenol is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill.

2. If in the solid form, 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.

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 collected and atomized in a suitable combustion chamber.

• Waste disposal methods:

Phenol may be disposed of:

1. If in the solid form, by making packages of phenol in paper or other flammable material and burning in a suitable combustion chamber, or by dissolving phenol in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

2. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill, or by atomizing the liquid in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PHENOL

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor or Particulate Concentration	
50 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.
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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of phenol; 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-Phenylene Diamine

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: $C_6H_8N_2$
- Synonyms: p-Diaminobenzene; 1,4-diaminobenzene
- Appearance: White to light purple or brown solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-phenylene diamine is 0.1 milligram of p-phenylene diamine per cubic meter of air (mg/m³) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Phenylene diamine 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: p-Phenylene diamine may cause irritation of the throat.

2. Long-term Exposure: Repeated or prolonged exposure may cause allergy with asthma or 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-phenylene diamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-phenylene diamine 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 p-phenylene diamine would be expected to be at increased risk from exposure. Examination of the respiratory 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**

p-Phenylene diamine dust is a skin and respiratory system sensitizer and may produce bronchial asthma and dermatitis in exposed workers. In cats, the minimal fatal peroral dose was 0.1 g/kg. Solutions administered orally or parenterally to animals caused a peculiar and selective edema of the conjunctivae, nose, lips, tongue, and neck. Inflammatory reactions of the pharynx and larynx have been reported in workers. Very small quantities of the dust have caused asthmatic attacks in workers after periods of exposure ranging from 3 months to 10 years. A dilute aqueous solution placed in the eye of a rabbit caused mild transient conjunctival edema. This compound may cause contact dermatitis through sensitization.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 108.1
2. Boiling point (760 mm Hg): 267 C (512 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of p-phenylene diamine): 3.71
5. Melting point: 141 C (286 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 4.7
8. Evaporation rate (butyl acetate = 1): Data not

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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available

- **Reactivity**

1. Conditions contributing to instability: Heat; light
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving p-phenylene diamine.
4. Special precautions: None

- **Flammability**

1. Flash point: 155.5 C (312 F) (closed cup)
2. Autoignition temperature: Data not available
3. Minimum explosive concentration: 0.025 g/l
4. Extinguishant: Carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of p-phenylene diamine.
2. Eye Irritation Level: Gleason reports that p-phenylene diamine in the eye produces "chemosis, lacrimation, exophthalmos ophthalmia, and even permanent blindness." Kirk and Othmer report that p-phenylene diamine "is responsible for keratoconjunctivitis, swollen conjunctiva, and eczema of the eyelids." Grant provides similar information, but no quantitative data are given.
3. Evaluation of Warning Properties: p-Phenylene diamine is treated as material with poor warning properties, since no quantitative data are available relating warning properties to air concentrations of p-phenylene diamine.

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

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 p-phenylene diamine 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 p-phenylene diamine or liquids containing p-phenylene diamine, where skin contact may occur.
- If employees' clothing may have become contaminated with p-phenylene diamine or liquids containing p-phenylene diamine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with p-phenylene diamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of p-phenylene diamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-phenylene diamine, the person performing the operation should be informed of p-phenylene diamine's hazardous properties.
- Non-impervious clothing which becomes contaminated with p-phenylene diamine should be removed promptly and not reworn until the p-phenylene diamine is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where p-phenylene diamine or liquids containing p-phenylene diamine may contact the eyes.

SANITATION

- Workers subject to skin contact with p-phenylene diamine or liquids containing p-phenylene diamine should wash with soap or mild detergent and water any areas of the body which may have contacted p-phenylene diamine at the end of each work day.
- Skin that becomes contaminated with p-phenylene diamine should be promptly washed or showered with soap or mild detergent and water to remove any p-phenylene diamine.

• Eating and smoking should not be permitted in areas where p-phenylene diamine or liquids containing p-phenylene diamine are handled, processed, or stored.
• Employees who handle p-phenylene diamine or liquids containing p-phenylene diamine 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-phenylene diamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in dye and dyestuff intermediates for fur, hair, leather, cotton, and synthetics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in photographic application as a fine-grain developing agent, for preparation of color developers, and for photochemical measurements; use in polymer technology for manufacture of Fiber B, and as a cross-linking agent; use as a catalyst; use in preparation of epoxy resins, synthetic fibers, heat-resistant polymers, and coatings for leather, paper, and textiles	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in rubber technology for natural and synthetic rubber for vulcanization, as an antioxidant, accelerator, and stabilizer	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis in preparation of antioxidants for petroleum fuels; preparation of grease thickeners, electrical insulators, and rust removers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in laboratory as an analytical reagent, and as a special solvent	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 p-phenylene diamine or liquids containing p-phenylene diamine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If p-phenylene diamine or liquids containing p-phenylene diamine get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If p-phenylene diamine or liquids containing p-phenylene diamine penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of p-phenylene diamine, 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-phenylene diamine 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 DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
• If p-phenylene diamine 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-Phenylene diamine may be disposed of:

1. By making packages of p-phenylene diamine 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-phenylene diamine 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-PHENYLENE DIAMINE

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate or Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25 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 25 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 p-phenylene diamine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Phenyl 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: $(C_6H_5)_2O$
- Synonyms: Diphenyl ether; diphenyl oxide
- Appearance and odor: Colorless solid or liquid with a somewhat disagreeable odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phenyl ether is 1 part of phenyl ether per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7 milligrams of phenyl ether per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phenyl 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 phenyl ether vapor or mist may cause nausea and irritation of the eyes and nose.

2. Long-term Exposure: Prolonged or repeated exposure to undiluted phenyl ether 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 phenyl ether.

- **Recommended medical surveillance**

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

—Skin disease: Phenyl 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 phenyl 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 phenyl 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 phenyl 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**

Phenyl ether irritates the skin and eyes and has an objectionable odor which may cause nausea. The liquid appears to be low in oral toxicity, but little information on its physiologic effects is available. The acute lethal dose for rats and guinea pigs is 4 g/kg. Animals that survived oral doses of 1 to 2 g/kg showed some injury to the liver, kidneys, spleen, and thyroid. 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: 170.2
2. Boiling point (760 mm Hg): 259 C (498 F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of phenyl ether): 5.86
5. Melting point: 27 C (81 F) (maximum value)
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): 0.0021
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 phenyl ether.
4. Special precautions: Phenyl ether will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 115 C (239 F) (closed cup)
2. Autoignition temperature: 620 C (1148 F)
3. Flammable limits in air, % by volume: Lower: 0.8; Upper: 1.5
4. Extinguishant: Foam dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: May reports an odor threshold for phenyl ether of 0.01 ppm, and Stern reports 0.001 ppm
2. Eye Irritation Level: The *Documentation of TLV's* states that "effects of . . . eye application (of phenyl ether) resemble closely those found for the eutectic mixture with diphenyl; phenyl ether in concentrated, prolonged exposures is somewhat irritating but is not so in dilution." The phenyl ether-diphenyl mixture is known to produce eye irritation at 3-4 ppm (Grant).
3. Evaluation of Warning Properties: Since the odor threshold of phenyl ether is lower than the permissible exposure limit, this substance 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 phenyl 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 phenyl ether may be used. An analytical method for phenyl 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 or solid phenyl ether.
- Non-impervious clothing which becomes contaminated with liquid or solid phenyl ether should be removed promptly and not reworn until the phenyl ether is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid phenyl ether may contact the eyes.

SANITATION

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

Operation	Controls
Use as a high-temperature, heat-transfer medium as Dowtherm A, Thermax, Diphyl, and Gilotherm	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as an organic intermediate in organic synthesis resulting in epoxy resins, other phenol-based heat-resistant resins, polysulfone resins, high-temperature lubricants, surfactants, specialty plasticizers, varnishes, phenol-formaldehyde resins, artificial sweetners, insecticides, preservatives, fire retardants, and adhesives	General dilution ventilation; personal protective equipment
Use as an odorant in the manufacture of soaps and perfumes; use as a flavoring agent in manufacture of food products	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 phenyl 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 phenyl ether gets on the skin, promptly wash the contaminated skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleanser. If phenyl ether soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleansers. If irritation persists after washing, get medical attention.

• **Breathing**

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

1. Ventilate area of spill or leak.
2. For small quantities, absorb or scoop up on paper. 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; however, if this is not practical, collect, dissolve in an appropriate solvent, and atomize in a suitable combustion chamber.

• Waste disposal method:

Phenyl ether may be disposed of by dissolving in appropriate solvent and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PHENYL ETHER

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s) with a full facepiece and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister with a full facepiece 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.
100 ppm or less	A powered air-purifying chemical cartridge respirator with a full facepiece, organic vapor cartridge, and 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 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 Phenyl Ether-Biphenyl 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: $(C_6H_5)_2O$ and $C_6H_5C_6H_5$
- Synonyms: Dowtherm A; diphenyl oxide-diphenyl mixture
- Appearance and odor: Straw-colored liquid that darkens on use with an aromatic, somewhat disagreeable odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phenyl ether-biphenyl mixture is 1 part of phenyl ether-biphenyl mixture per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7 milligrams of phenyl ether-biphenyl mixture 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 phenyl ether-biphenyl mixture from 1 ppm to 0.5 ppm as a vapor.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phenyl ether-biphenyl mixture 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 phenyl ether-biphenyl mixture may cause irritation of the eyes, nose, and skin. It may also cause nausea.

2. Long-term Exposure: Repeated or prolonged contact 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 phenyl ether-biphenyl mixture.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phenyl ether-biphenyl mixture 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 phenyl ether-biphenyl mixture exposure.

—Skin disease: Phenyl ether-biphenyl mixture 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 phenyl ether-biphenyl mixture 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 phenyl ether-biphenyl mixture 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 phenyl ether-biphenyl mixture 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**

Phenyl ether-biphenyl mixture is primarily an irritant to

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 eyes, skin, and upper respiratory tract. Repeated 8-hour exposures at 182 mg/m³ of a vapor-mist mixture were lethal to some animals within 1-½ months. Long-term (6-month) studies of four species at 7 to 10 ppm showed no significant adverse effects, although these concentrations are extremely nauseating to human subjects and painfully irritating to the eyes and nose. While 1 ppm is tolerable to most individuals, the odor at 0.1 ppm may be objectionable to some. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 166 (average)
2. Boiling point (760 mm Hg): 257 C (495 F)
3. Specific gravity (water = 1): 1.05 to 1.07
4. Vapor density (air = 1 at boiling point of phenyl ether-biphenyl mixture): 5.7 (average)
5. Melting point: 12 C (54 F)
6. Vapor pressure at 25 C (77 F): 0.08 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0014
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 phenyl ether-biphenyl mixture.
4. Special precautions: Phenyl ether-biphenyl mixture will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 124 C (255 F) (open cup)
2. Autoignition temperature: 621 C (1150 F)
3. Flammable limits in air, % by volume: Lower: 0.5; Upper: 6.2 (at 500 F)
4. Extinguishant: Foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states, "Experience with human subjects has indicated that concentrations of vapors of Dowtherm A ranging from 0.1 to 1 ppm are readily detected by the olfactory organs and are unpleasant, sometimes producing nausea." The *Documentation of TLV's* states that a TLV of 1 ppm is recommended "to prevent disagreeable, nauseating odor for the majority of exposed workers. As little as 0.1 ppm may be objectionable to some sensitized, exposed individuals. The TLV of 1 ppm is sufficiently low to prevent serious toxic effects but may not eliminate all objectionable symptoms."
2. Irritation Levels: Grant states that "when concentrations of 3 or 4 ppm in air are reached, there is irritation of the eyes, nose, and throat."
3. Evaluation of Warning Properties: Through its odor and irritant effects, phenyl ether-biphenyl mixture can be detected at a concentration within 3 times the permissible exposure limit. For the purposes of this guideline, this mixture 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 phenyl ether-biphenyl mixture in an adsorption tube containing silica gel, followed by desorption with benzene, and gas chromatographic analysis. An analytical method for phenyl ether-biphenyl mixture 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 or solid phenyl ether-biphenyl mixture.
• Non-impervious clothing which becomes contaminated with liquid or solid phenyl ether-biphenyl mixture should be removed promptly and not reworn until the phenyl ether-biphenyl mixture is removed from the clothing.
• Employees should be provided with and required to use dust- and splash-proof safety goggles where liquid or solid phenyl ether-biphenyl mixture may contact the eyes.

SANITATION

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

Operation	Controls
Use in chemical, petroleum, and nuclear industry as a high-transfer medium used in heating and cooling processes – marked as Dowtherm A, Termax, Diphyl, and Gilotherm	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a dye carrier (dyeing aid) for printing and dyeing polyester textiles	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 phenyl ether-biphenyl mixture 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 phenyl ether-biphenyl mixture gets on the skin, promptly wash the contaminated skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleansers. If phenyl ether-biphenyl mixture soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent together with powdered pumice, borax, or other suitable cleaners. If irritation persists after washing, get medical attention.
• **Breathing**
If a person breathes in large amounts of phenyl ether-biphenyl 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.
• **Swallowing**
When phenyl ether-bisphenyl mixture 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 phenyl ether-biphenyl mixture is spilled or leaked, the following steps should be taken:
1. Ventilate area of spill or leak.
2. For small quantities, absorb or scoop up on paper. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities may be reclaimed; however, if this is not practical, dissolve in an appropriate solvent and atomize in a suitable combustion chamber.
• Waste disposal method:
Phenyl ether-biphenyl mixture may be disposed of by dissolving in an appropriate solvent and atomizing in a suitable combustion chamber.

REFERENCES

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

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RESPIRATORY PROTECTION FOR PHENYL ETHER-BIPHENYL MIXTURE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s) with a full facepiece and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister with a full facepiece 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.
100 ppm or less	A powered air-purifying chemical cartridge respirator with a full facepiece, organic vapor cartridge, and 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 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.

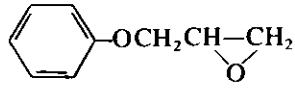
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PHENYL GLYCIDYL ETHER

INTRODUCTION

This guideline summarizes pertinent information about phenyl glycidyl ether (PGE) 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:** $C_9H_{10}O_2$
- **Structure:**



- **Synonyms:** Glycidyl phenyl ether; PGE; phenyl 2,3-epoxypropyl ether; 1,2-epoxy-3-phenoxypropane; phenoxy-propene oxide
- **Identifiers:** CAS 122-60-1; RTECS TZ3675000; DOT not assigned
- **Appearance:** Colorless liquid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 150.17
2. Boiling point (at 760 mmHg): 245°C (473°F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of PGE): 4.37
5. Melting point: 3.5°C (38°F)
6. Vapor pressure at 25°C (77°F): 0.01 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.24
8. Saturation concentration in air (approximate) at 25°C (77°F): 0.0013% (13 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with amines, strong acids, and strong bases may cause polymerization with the liberation of heat and spattering. Exposure to light and air may result in the formation of explosive peroxides.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving PGE.
3. Caution: PGE will cause some forms of plastics, coatings, and rubber to deteriorate.

- **Flammability**

1. Flash point: 120°C (248°F) (closed cup)
2. Extinguishant: Dry chemical, carbon dioxide, or alcohol foam
3. Class IIIB Combustible Liquid (29 CFR 1910.106)

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, PGE should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for PGE is 10 parts of PGE per million parts of air (ppm) [60 milligrams of PGE per cubic meter air (mg/m³)] as a time-weighted average (TWA) concentration over an 8-hour workshift. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 1 ppm (5 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 1 ppm (6 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

Table 1.—Occupational exposure limits for phenyl glycidyl ether

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	10	60
NIOSH REL, ceiling (15 min)	1	5
ACGIH TLV® TWA	1	6

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HEALTH HAZARD INFORMATION

• **Routes of exposure**

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

• **Summary of toxicology**

Effects on animals: Acute dermal or oral administration of PGE to rats and mice caused tissue destruction (necrosis) at the site of administration, liver damage, and central nervous system (CNS) depression. Subchronic inhalation of PGE by rats produced equivocal evidence of testicular degeneration. Chronic inhalation of PGE by rats produced nasal cancer. NIOSH will continue to monitor the research regarding PGE to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.

• **Signs and symptoms of exposure**

1. *Short-term (acute):* Exposure to PGE can cause irritation of the eyes, nose, respiratory tract, and skin.
2. *Long-term (chronic):* Exposure to PGE can cause defatting and drying of the skin, dermatitis, blisters, edema, rash, eczema, and skin sensitization; cross sensitization with other glycidyl ethers 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 PGE, 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 PGE 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 PGE. 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 reproductive, 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 PGE. 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 PGE 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 PGE may also be used if available. A detailed sampling and analytical method for PGE may be found in the *NIOSH Manual of Analytical Methods* (method number S74).

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 PGE.

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

SANITATION

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

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

Skin that becomes contaminated with PGE 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 PGE 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 PGE 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 phenyl glycidyl ether

Operations	Controls
During use as a coupling agent, catalyst, or reactive diluent in curing rubber, thermostable epoxy resins, tire cord, and electric insulating materials	Process enclosure, local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a stabilizer of halogenated compounds; during use in the treatment of fabric	Local exhaust ventilation, general dilution ventilation, personal protective equipment
During use as a copolymer in the production of epoxy polymers; during use as chemical intermediate	Process enclosure, local exhaust ventilation, general dilution 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 PGE, an eye-wash fountain should be provided within the immediate work area for emergency use.

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

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

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 25 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 50 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 500 ppm	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown concentrations or levels above 500 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor canister
	Any appropriate escape-type self-contained breathing apparatus

* Only NIOSH/MSHA-approved equipment should be used.
† The respiratory protection listed for any given condition is the minimum required to meet the NIOSH REL of 1 ppm (5 mg/m³) (ceiling).

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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PHENYLHYDRAZINE

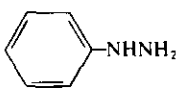
POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about phenylhydrazine 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:** $C_6H_8N_2$
- **Structure:**



- **Synonyms:** Hydrazinobenzene, hydrazine-benzene
- **Identifiers:** CAS 100-63-0; RTECS MV8925000; DOT 2572, label required: "Poison"
- **Appearance and odor:** Pale yellow crystals or oily liquid with a faint aromatic odor; color darkens upon exposure to air and light

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 108.16
2. Boiling point (at 760 mmHg): 243.5°C (471°F) with decomposition
3. Specific gravity (water = 1): 1.0978
4. Vapor density (air = 1 at boiling point of phenylhydrazine): 3.7
5. Melting point: 19.6°C (68°F)
6. Vapor pressure at 25°C (77°F): 0.04 mmHg
7. Slightly soluble in water
8. Evaporation rate (butyl acetate = 1): 0.4
9. Saturation concentration in air (approximate) at 25°C (77°F): 50 ppm
10. Ionization potential: 7.66 eV

- **Reactivity**

1. Incompatibilities: Phenylhydrazine 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 phenylhydrazine.
3. Caution: Phenylhydrazine will attack cork, some forms of plastics, coatings, and rubber.

- **Flammability**

1. Flash point: 88°C (190°F) (closed cup)
2. Autoignition temperature: 174°C (345°F)
3. Extinguishant: Alcohol foam, dry chemical, carbon dioxide, or large quantities of coarse water spray
4. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (NFPA)
5. Caution: Phenylhydrazine 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**

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 phenylhydrazine is 5 parts of phenylhydrazine per million parts of air (ppm) [22 milligrams of phenylhydrazine 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 phenylhydrazine 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 0.14 ppm (0.6 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 Conference of Governmental Industrial Hygienists (ACGIH) has designated phenylhydrazine as an A2 substance (suspected hu-

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man carcinogen) having an assigned threshold limit value (TLV®) of 5 ppm (20 mg/m³) (Skin) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short term exposure limit (STEL) is 10 ppm (45 mg/m³) (Table 1).

Table 1.— Occupational exposure limits for phenylhydrazine

	Exposure limits ppm	mg/m³
OSHA PEL TWA (Skin)*	5	22
NIOSH REL (Ca)†		
ceiling (120 min)	0.14	0.6
ACGIH TLV® TWA (Skin)		
(A2)§	5	20
STEL (Skin) (A2)	10	45

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

• Summary of toxicology
1. *Effects on animals:* Acute subcutaneous or intraperitoneal injection of phenylhydrazine hydrochloride in mice, rats, or dogs caused deficient oxygenation of the blood (cyanosis), breathing difficulty (dyspnea), convulsions, severe hemolytic anemia, or degenerative lesions of the liver and kidneys. Subchronic oral administration of phenylhydrazine to mice produced tumors of the blood vessels and cancer of the lungs. Phenylhydrazine injected into pregnant rats reduced certain learning abilities in the offspring by inducing severe neonatal jaundice and anemia.
2. *Effects on humans:* Exposure of workers to phenylhydrazine has caused hemolytic anemia.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to phenylhydrazine can cause vomiting, diarrhea, fatigue, headache, and irritation and itchiness of the eyes and skin.
2. *Long-term (chronic):* Repeated skin contact with phenylhydrazine can cause skin sensitization and eczematous dermatitis with redness, swelling, and rash.

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 phenylhydrazine, 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 workers 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 phenylhydrazine 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 phenylhydrazine.

• Periodic medical screening and/or biologic monitoring
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examina-

tions may be necessary should a worker develop symptoms that may be attributed to exposure to phenylhydrazine. 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 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 phenylhydrazine 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 phenylhydrazine. 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 phenylhydrazine with tubes containing sulfuric-acid-coated silica and analyzing by gas chromatography. Direct-reading devices calibrated to measure phenylhydrazine may also be used if available. A detailed sampling and analytical method for phenylhydrazine 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 phenylhydrazine.

SANITATION

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

Operations	Controls
During the manufacture of phenylhydrazine; during maintenance of manufacturing and storage equipment	Process enclosure, local exhaust ventilation, personal protective equipment
During use in the manufacture of pharmaceuticals, photographic developers, polymethene dyes, and nitron (a stabilizer for explosives)	Process enclosure, local exhaust ventilation, personal protective equipment
During use as an analytical reagent, intermediate in inorganic synthesis, or reducing 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 phenylhydrazine, an eye-wash fountain should be provided within the immediate work area for emergency use.

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

If phenylhydrazine gets on the skin, wash it immediately with soap and water. If phenylhydrazine 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 phenylhydrazine 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 phenylhydrazine 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 phenylhydrazine may be diluted with water and flushed to a safe, open area such as a catch basin. Phenylhydrazine 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 phenylhydrazine

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 Phosdrin

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: $(CH_3O)_2PO_2C(CH_3)=CHCOOCH$
- Synonyms: Mevinphos (R); 2-carbomethoxy-1-methylvinyl dimethyl phosphate
- Appearance and odor: Colorless or yellow liquid with a weak odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosdrin is 0.1 milligram of phosdrin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosdrin 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: After inhalation of phosdrin, 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 phosdrin, 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 phosdrin 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 phosdrin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosdrin 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: Phosdrin (Mevinphos) 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**

Phosdrin (Mevinphos) 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 several 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 two cases of moderate intoxication from Mevinphos, urinary excretion of dimethylphosphate (a metabolite of Mevinphos) was almost complete 50 hours after exposure; although a number of other organophosphorus pesticides also yield dimethylphosphate, the presence of significant amounts of this metabolite in the urine may be useful in estimating the absorption of Mevinphos.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 224
2. Boiling point (760 mm Hg): 325 C (617 F)
3. Specific gravity (water = 1): 1.24
4. Vapor density (air = 1 at boiling point of phosdrin): Not applicable
5. Melting point: −56 C (−69 F) (pour point)
6. Vapor pressure at 20 C (68 F): 0.003 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): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Phosdrin decomposes vigorously when heated above 300 C (572 F) and will 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 phosphoric acid mist and carbon monoxide) may be released in a fire involving phosdrin.
4. Special precautions: Phosdrin will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 79 C (175 F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of phosdrin.
2. Eye Irritation Level: Phosdrin 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, phosdrin is treated as a material with poor warning properties. The concentration of phosdrin 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 phosdrin 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 phosdrin.

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

• Where there is any possibility of exposure of an employee's body to phosdrin, 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 phosdrin should be removed immediately and not reworn until the phosdrin 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 phosdrin contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to phosdrin, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

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

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

Operation	Controls
Application as an insecticide on agricultural crops, fruits, and vegetables; for ornamentals in greenhouses; use as an insecticide in sewage treatment plants	Personal protective equipment
Formulation and mixing for insecticidal application	Local exhaust ventilation; personal protective equipment
Manufacture of phosdrin	Local exhaust ventilation; personal protective equipment; 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 phosdrin or phosdrin 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 phosdrin or phosdrin mists get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If phosdrin or phosdrin 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 phosdrin, 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 phosdrin 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 phosdrin 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:

Phosdrin 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 PHOSDRIN

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate or Vapor Concentration	
1mg/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.
40 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any 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 phosdrin; 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 40 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Phosgene

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: $COCl_2$
- Synonyms: Carbonyl chloride; carbon oxychloride; chloroformyl chloride
- Appearance and odor: Colorless liquid or gas with a sweet odor like hay at low concentrations and a sharp pungent odor at high concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosgene is 0.1 part of phosgene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of phosgene per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 0.1 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 0.2 ppm averaged over a 15-minute period. The NIOSH Criteria Document for Phosgene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosgene 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: Phosgene, after a minute or so of exposure to low concentrations, may cause cough and discomfort in the chest and irritation of the nose and throat. Higher concentrations may cause painful coughing with respiratory irritation. Phosgene may cause pulmonary edema with coughing, shortness of breath, and production of frothy sputum. This can be fatal. Pulmonary edema may occur many hours after exposure. The gas may irritate the eyes. If liquid phosgene is splashed on the skin or eyes, it may cause burns.

2. Long-term Exposure: No known effect

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 phosgene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosgene 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: Phosgene may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec and 25— 75): Phosgene is reported to cause pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Phosgene gas is a severe respiratory irritant. The least concentration claimed to be capable of causing immediate irritation of the human throat is 3 ppm; 4 ppm causes immediate irritation of the eyes; 4.8 ppm causes cough; brief exposure to 50 ppm may be rapidly fatal. With moderate exposure, the presenting symptoms are often a dryness or a burning sensation in the throat, vomiting, pain in the chest, and dyspnea. The onset of symptoms

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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 severe respiratory distress may be delayed for up to 72 hours, the latent interval depending upon the concentration and duration of exposure. The delayed onset of pulmonary edema is characterized by cough, abundant quantities of foamy sputum, progressive dyspnea, and severe cyanosis. Pulmonary edema may progress to pneumonia, and cardiac failure may intervene. The gas in concentrations of 1 to 2 ppm causes eye discomfort, and higher concentrations are likely to cause lacrimation and conjunctivitis; splashes of liquid phosgene in the eye may produce severe irritation. Skin contact with the liquid may cause severe burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98.9
2. Boiling point (760 mm Hg): 8.2 C (46.7 F)
3. Specific gravity (water = 1): 1.4
4. Vapor density (air = 1 at boiling point of phosgene): 3.4
5. Melting point: −128 C (−198 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
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with moisture causes slow decomposition to form hydrogen chloride with carbon dioxide.
3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine and carbon monoxide) may be released when phosgene decomposes, but these gases are less toxic than phosgene itself.
4. Special precautions: Liquid phosgene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: The odor threshold of phosgene has been reported as 0.125 ppm by the ILO, 0.5 to 1.0 ppm by Thienes and Haley, and 0.5 ppm by both Patty and May. The M*CA states in its Chemical Safety Data Sheet*, however, that "the gas has the ability to condition the sense of smell so that the characteristic odor can be detected only briefly at the time of initial exposure."
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "the vapor of phosgene in concentrations of 1 to 2 ppm causes a scratchy sensation of the eyes, and higher concentrations are likely to cause lacrimation and conjunctivitis." They also state that within a few minutes 5 ppm might cause eye irritation.
3. Other Information: Patty notes that concentrations below 10 ppm produce mild irritation of the mucous membranes, and concentrations above 10 ppm can produce serious irritation. At 2 ppm, irritation of the nose and throat is "barely detectable." The *Documentation of TLV's* reports that 3 ppm has been claimed to be the lowest concentration causing irritation of the throat. Stecher notes, however, that phosgene is "an insidious poison, as it is not irritating immediately, even when fatal concentrations are inhaled."
4. Evaluation of Warning Properties: Since phosgene has the ability "to condition the sense of smell so that the characteristic odor can be detected only briefly at the time of initial exposure," and since the threshold of eye, nose, and throat irritation are many times higher than the permissible exposure limit, phosgene has been treated as a material with poor warning properties. In addition, according to Stecher, the irritant effects of phosgene are delayed, giving no warning that harmful concentrations are being inhaled.

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 phosgene. 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 phosgene in a midget impinger containing a solution of nitrobenzylpyridine, followed by colorimetric analysis. An analytical method for phosgene 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, full facepiece respirator, gloves, face shields (eight-inch minimum), and other appropriate protective clothing where skin contact with liquid phosgene may occur.

• Where there is any possibility of exposure of an employee's body to liquid phosgene, 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 liquid phosgene should be removed immediately while using quick drenching facilities and not reworn until the phosgene 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 phosgene contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to phosgene, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes wet with liquid phosgene should be immediately washed or showered with very large quantities of water to remove any phosgene.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during open-flame cutting of certain metals in presence of chlorinated hydrocarbons	Insolation of operations from chlorinated hydrocarbons; local exhaust ventilation; personal protective equipment
Liberation from synthesis of isocyanates in manufacture of polyurethane plastics; alkyl isocyanates in pesticide manufacture; polycarbonated resins for molded plastics, dyestuffs, and pharmaceuticals	Process enclosure; local exhaust ventilation
Liberation during fire-extinguishing with agents containing chlorinated hydrocarbons	Material substitution; personal protective equipment
Liberation during sand bleaching operations in glass manufacture	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 phosgene 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 phosgene gets on the skin, immediately flush the contaminated skin with large quantities of water. If phosgene soaks through the clothing, remove the clothing immediately while using a quick drenching facility and flush the skin with large quantities of water. If irritation persists after washing, get medical attention.

• **Breathing**

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

1. Ventilate area of spill or leak.
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. Water spray may be used to knock down the vapor.
3. If in the liquid form, allow to vaporize.

• Waste disposal methods:

Phosgene 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.

ADDITIONAL INFORMATION

To find additional information on phosgene, look up phosgene in the following documents:

• Medical Surveillance for Chemical Hazards

• Respiratory Protection for Chemical Hazards

• Personal Protection and Sanitation for Chemical Hazards

• NIOSH Criteria Document for Phosgene (February 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR PHOSGENE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1 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 phosgene. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Phosphine

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: PH_3
- Synonyms: Hydrogen phosphide; phosphorus hydride; phosphorated hydrogen
- Appearance and odor: Colorless gas with a characteristic fishy odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphine is 0.3 part of phosphine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of phosphine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphine can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of phosphine may cause coughing, shortness of breath, and severe breathing difficulty. This breathing difficulty may not appear until several hours after exposure has ceased. It may also cause thirst, nausea, vomiting, stomach pain, diarrhea, back pain, a feeling of coldness, fainting, and death.

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 phosphine.

- **Recommended medical surveillance**

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

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

Phosphine gas is a severe pulmonary irritant and an acute systemic poison; it has caused both sudden death and delayed death due to pulmonary edema. Workers exposed intermittently to concentrations up to 35 ppm, but averaging below 10 ppm, complained of nausea, vomiting, diarrhea, chest tightness and cough, headache, and dizziness; no evidence of cumulative effects was noted. Single severe exposures cause similar signs and symptoms, as well as excessive thirst, muscle pain, chills, sensation of pressure in the chest, dyspnea, syncope, and stupor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 34.04
2. Boiling point (760 mm Hg): −87.8 C (−126 F)
3. Specific gravity (water = 1): Liquid = 0.75 at boiling point
4. Vapor density (air = 1 at boiling point of phosphine): 1.17
5. Melting point: −134 C (−209 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere

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

7. Solubility in water, g/100 g water at 20 C (68 F): 0.04

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Overheated cylinders may explode.

2. Incompatibilities: Contact with air or any other oxidizer such as chlorine, etc., will cause ignition of phosphine. Phosphine reacts with acids, halogenated hydrocarbons, and moisture.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of phosphorus, phosphoric acid mist, and hydrogen) may be released in a fire involving phosphine.

4. Special precautions: Phosphine is an unusually reactive and poisonous substance, and is usually handled in small quantities only.

• **Flammability**

1. Flash point: Not applicable

2. Autoignition temperature: Spontaneously flammable at room temperature

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

4. Extinguishant: Shut off flow of gas. Carbon dioxide may extinguish the fire, but it will re-ignite spontaneously. If the fire is in a safe location, let the fire burn.

• **Warning properties**

1. Odor Threshold: May reports an odor threshold for phosphine of 0.02 ppm. Although Patty states that the limit of perceptibility is 1.5 to 3.0 ppm, the experience of industrial users confirms the odor threshold given by May.

2. Eye Irritation Level: Grant states that "although numerous instances of poisoning of human beings and experimental animals (from phosphine) have been reported, no characteristic ocular or visual effects are known."

3. Evaluation of Warning Properties: Since the odor of phosphine can be detected at a concentration well 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**

An analytical method for phosphine 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 phosphine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a doping agent in manufacture of solid-state components for electronic circuits and in manufacture of lasers	Local exhaust ventilation; personal protective equipment
Use in preparation of alkyl and aryl phosphonium halides in textile treatment; use in organic intermediates; use as curing catalysts for epoxy resins, polymerization initiators, and condensation catalysts	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a fumigant for stored grain	Local exhaust ventilation; personal protective equipment

Liberation during drilling, machining, and grinding of ductile iron; during quenching of alloys or sludges; during cleaning of rusty metal in phosphoric acid; and during welding of steel coated with phosphate rust-proofing agents	Local exhaust ventilation; personal protective equipment
Liberation during manufacture and use of acetylene; during extraction of phosphorus, and use of inorganic phosphorus compounds use of phosphorus sesquisulfide in manufacture of safety matches and calcium phosphide in pyrotechnics	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 phosphine, 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 phosphine 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.

• Waste disposal method:

Phosphine 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: "Phosphine," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• American Industrial Hygiene Association: "Phosphine," *Hygienic Guide Series*, Detroit, Michigan, 1964.

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RESPIRATORY PROTECTION FOR PHOSPHINE

Condition	Minimum Respiratory Protection* Required Above 0.3 ppm
Gas Concentration	
3 ppm or less	Any chemical cartridge respirator with a cartridge(s) providing protection against phosphine. Any supplied-air respirator. Any self-contained breathing apparatus.
15 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) providing protection against phosphine. A gas mask with a chin-style or a front- or back-mounted canister providing protection against phosphine. 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 operated in pressure-demand or other positive pressure or 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 phosphine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Phosphoric 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: H_3PO_4
- Synonyms: White phosphoric acid; ortho-phosphoric acid; 85% phosphoric acid; meta-phosphoric acid
- Appearance and odor: Viscous, colorless, odorless liquid which can solidify at temperatures below 21 C (70 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphoric 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: Solid phosphoric acid or its solutions may cause skin burns. Contact with the eyes may produce irritation and eye burns. Exposure to phosphoric acid vapor or mist may cause irritation of the eyes, nose, and throat.

2. Long-term Exposure: Repeated or prolonged exposure 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 phosphoric acid.

- **Recommended medical surveillance**

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

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

—Skin disease: Phosphoric acid dust, mist, or solutions may 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**

Phosphoric acid mist is an irritant to the eyes, upper respiratory tract, and skin. The solid is especially irritating to skin in the presence of moisture. Unacclimated workers could not endure exposure to fumes of phosphorus pentoxide (the anhydride of phosphoric acid) at a concentration of 100 mg/m^3; exposure to concentrations between 3.6 and 11.3 mg/m^3 produced coughing. Concentrations of 0.8 to 5.4 mg/m^3 were noticeable but not uncomfortable. There is no evidence that phosphorus poisoning can result from contact with phosphoric acid. The risk of pulmonary edema resulting from the inhalation of mist or spray is remote. A dilute solution buffered to pH 2.5 caused a moderate brief stinging sensation but no injury when dropped in the human eye. A 75% solution will cause severe skin burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98

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): 260 C (500 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of phosphoric acid): 3.4
5. Melting point: 21 C (70 F)
6. Vapor pressure at 20 C (68 F): 0.0285 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): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong caustics can cause liberation of much heat and violent spattering. Contact with most metals causes formation of flammable and explosive hydrogen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume) may be released when phosphoric acid decomposes.
4. Special precautions: Liquid phosphoric acid will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Phosphoric acid mist can cause irritation of the eyes and respiratory tract, according to the *Hygienic Guide*. No quantitative information is given, however. Deichmann and Gerarde note that since phosphoric acid "has a low vapor pressure at room temperature, it is not irritating to the eyes or respiratory tract, unless introduced into the atmosphere as a spray or mist."

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 phosphoric acid on a cellulose membrane filter, followed by leaching with hot water, chemical reaction, and spectrophotometric analysis. An analytical method for phosphoric acid 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 solid or liquid phosphoric acid or solutions containing greater than 1.6% ortho-phosphoric acid by weight or any concentration of meta-phosphoric acid.

• 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 1.6% or less ortho-phosphoric acid by weight.

• If employees' clothing may have become contaminated with solid phosphoric acid, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where there is any possibility of exposure of an employee's body to solid or liquid phosphoric acid or solutions containing phosphoric 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 phosphoric acid should be removed immediately and not reworn until the phosphoric acid 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 phosphoric acid or solutions containing phosphoric acid contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to solid or liquid phosphoric acid or solutions containing more than 1.6% ortho-phosphoric acid by weight, or any concentration of meta-phosphoric acid, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in manufacture of aluminum products in bright dipping operations; use in cleaning, electropolishing, and pickling in manufacture of steel, brass, bronze, and copper during surface treatment and rust-proofing operations	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of intermediates in manufacture of soil fertilizers; use in manufacture of livestock and poultry feed	Process enclosure; local exhaust ventilation; personal protective equipment
Use during synthesis of detergent and soap builders and water-treatment chemicals; use as an acidulant and flavor agent in manufacture of carbonated beverages and jellies and preserves	Process enclosure; personal protective equipment
Use in manufacture of food products, intermediates, and food additives; use as an antioxidant and preservative; use in wood, textile, polyurethane foam flame-retardant processing and production of flame-retardant agents	Process enclosure; personal protective equipment
Use in manufacture of cleaning preparations and disinfectants	Process enclosure; personal protective equipment
Use as a bonding agent in manufacture of refactory bricks; use during lithography and photoengraving operations	Process enclosure; personal protective equipment
Use as a catalyst in synthesis of other chemicals; use in synthesis of textile and leather processing chemicals, clays, ceramics, cements, and clay-thinning agents for drilling mud formulations	Process enclosure; personal protective equipment
Use in synthesis of pharmaceuticals and pharmaceutical intermediates and in the extraction of penicillin; use as a laboratory reagent	Process enclosure; personal protective equipment
Use during manufacture of opal glass; during manufacture of dental cements and dentrifice adhesives, adhesive gums, and synthetic rubber; and in the manufacture of electric lights	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 phosphoric acid 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 phosphoric acid gets on the skin, immediately flush the contaminated skin with water. If phosphoric acid soaks through the clothing, remove the clothing immediately and flush the skin with water.

• **Breathing**

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

1. Ventilate area of spill or leak.
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.
3. If in the liquid form, collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Liquid phosphoric acid may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and diposing in a secured sanitary landfill.

REFERENCES

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

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RESPIRATORY PROTECTION FOR PHOSPHORIC ACID

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate or Vapor Concentration	
50 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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

Occupational Health Guideline for Phosphorus (Yellow)

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: P_4
- Synonyms: White phosphorus; WP; phosphorus, elemental, white
- Appearance and odor: White to yellow, soft, waxy solid which gives off acrid fumes on exposure to air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphorus (yellow) is 0.1 milligram of phosphorus (yellow) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus (yellow) 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: The vapors of burning phosphorus (yellow) are irritating to the nose, throat, and lungs. Severe breathing difficulties may occur. The onset of these difficulties may be delayed for several hours. Phosphorus (yellow) on contact with the skin may ignite and produce severe skin burns with blistering. Phosphorus (yellow) is especially hazardous to the eyes and may produce severe damage. When phosphorus (yellow) is swallowed, after a delay of a few hours, nausea, vomiting, and abdominal pain may occur. The vomit may smell like garlic and glow in the dark. After 24 to 36 hours, the symptoms may go away. In a few hours or 2 or 3 days, the nausea, vomiting, and abdominal pain may reappear with diarrhea and a yellow color to the skin. Death may occur.

2. Long-term Exposure: Repeated or prolonged exposure to phosphorus (yellow) can cause "phossy jaw" with pain and swelling of the jaw, toothaches, loosening of the teeth and destruction of the jawbone. Chronic exposure to phosphorus (yellow) can also cause weakness, anemia, loss of appetite, stomach complaints, cough, and paleness. In addition, chronic exposure to phosphorus (yellow) may cause bones to become brittle and break.

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 phosphorus (yellow).

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus (yellow) 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. Particular attention should be given to the jaw and teeth. The skin should be examined for evidence of chronic disorders.

—Dental examination: Phosphorus exposure may aggravate existing dental disorders such as caries, periodontal disease, retained roots, and cysts which may predispose to toxic necrosis of the jaw. Dental examination including x-rays should be performed.

—Liver function tests: Since liver damage has been observed in humans exposed to phosphorus, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Complete blood count: Phosphorus exposure may cause anemia. A complete blood count should be per-

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 including red and white blood cell count, a differential count of a stained blood smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an semi-annual basis.

• **Summary of toxicology**

Yellow phosphorus fume irritates the respiratory tract and eyes; the solid in contact with the skin produces deep thermal burns; prolonged absorption of phosphorus causes necrosis of facial bones. Yellow phosphorus spontaneously burns in air, and the vapors released are irritating to the respiratory tract. The early signs of systemic intoxication by phosphorus are abdominal pain, jaundice, and a garlic odor of the breath; prolonged intake may cause anemia, cachexia, and necrosis of bone, typically the maxilla and mandible. Complaints of possible overexposure among phosphorus workers may be toothache and excessive salivation; there may be dull red appearance of the oral mucosa; one or more teeth may loosen, followed by pain and swelling of the jaw; healing may be delayed following dental procedures such as extractions; with necrosis of bone, sequestra may develop with sinus tract formation. In a series of 10 cases, the shortest period of exposure to phosphorus fume leading to bone necrosis was 10 months (2 cases) and the longest was 18 years. Yellow phosphorus fume causes severe eye irritation with blepharospasm, photophobia, and lacrimation; the solid in the eye produces severe injury. Phosphorus burns on the skin are deep and painful; a firm eschar is produced and is surrounded by vesiculation.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 123.9
2. Boiling point (760 mm Hg): 279 C (535 F)
3. Specific gravity (water = 1): 1.82
4. Vapor density (air = 1 at boiling point of phosphorus (yellow)): 4.4
5. Melting point: 44 C (111 F)
6. Vapor pressure at 20 C (68 F): 0.026 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0003
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Light causes formation of yellow or red color.
2. Incompatibilities: Contact with air and all oxidizing agents (including elemental sulfur) will cause fires and explosions. Contact with strong caustics will cause formation of poisonous and flammable phosphine gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume) may be released in a fire involving phosphorus (yellow).
4. Special precautions: Liquid phosphorus (yellow) will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Ignites spontaneously in air at or above 30 C (86 F)
2. Autoignition temperature: 30 C (86 F)
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Water, carbon dioxide, sand, warth, dry chemical

• **Warning properties**

Grant states that yellow phosphorus fumes are "irritating to the respiratory tract and cause severe ocular irritation with blepharospasm, photophobia, and lacrimation. Particles of white phosphorus (yellow phosphorus) are caustic and seriously damaging in contact with tissues."

No quantitative information is available concerning the concentrations that produce eye irritation, 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**

An analytical method for phosphorus (yellow) 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 flame-retardant clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid phosphorus (yellow).
- Clothing contaminated with phosphorus (yellow) should be placed underwater in closed containers for storage until it can be discarded or until provision is made for the removal of phosphorus (yellow) from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphorus (yellow), the person performing the operation should be informed of phosphorus (yellow)'s hazardous properties.
- Where there is any possibility of exposure of an employee's body to solid or liquid phosphorus (yellow), facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes contaminated with phosphorus (yellow) should be removed immediately and not reworn until the phosphorus (yellow) 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 phosphorus (yellow) contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid phosphorus (yellow), an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

Operation	Controls
Use in synthesis of high purity phosphoric acid salts for use as fertilizers, water treatment chemicals, food products, beverages, and dentrifices; use in synthesis of inorganic phosphorus compounds for use as pesticides, flame retardants for plastics and fibers, and gasoline and lube oil additives; use in synthesis of inorganic and organic compounds	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in manufacture of phosphorus alloys for introduction into low carbon steel, copper alloys, copper pipe, and bronze	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in manufacture of explosives, munitions, and pyrotechnics for military use	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst in synthesis of acrylonitrile and organic bromine compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during conversion of yellow phosphorus to red phosphorus for manufacture of wood and paper safety matches	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as an ingredient of rat poison and roach powders	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 phosphorus (yellow) 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 phosphorus (yellow) gets on the skin, immediately flush the contaminated skin with water. If phosphorus (yellow) penetrates through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately. The skin should be kept wet until medical attention is obtained to prevent any remaining phosphorus (yellow) from burning.

• **Breathing**

If a person breathes in large amounts of phosphorus (yellow), 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 phosphorus (yellow) 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 phosphorus (yellow) is spilled, the following step should be taken:

1. Immediately douse the spill with water and cover with wet sand or dirt.

• Waste disposal method:

Phosphorus (yellow), after solidification and covering with wet sand or dirt, may be disposed of in a secured sanitary landfill.

REFERENCES

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

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RESPIRATORY PROTECTION FOR PHOSPHORUS (YELLOW)

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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

Occupational Health Guideline for Phosphorus Pentachloride

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: PCl_5
- Synonyms: None
- Appearance and odor: Pale yellow solid with an odor like hydrochloric acid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus pentachloride 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 phosphorus pentachloride may cause irritation of the eyes and respiratory tract. Cases of bronchitis have resulted from exposure to this chemical. Severe breathing difficulties may occur. These breathing difficulties may be delayed in onset several hours after exposure has ceased. Phosphorus pentachloride on the skin may cause burning and irritation of the skin.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphorus pentachloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus pentachloride 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: Phosphorus pentachloride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Phosphorus pentachloride 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**

Phosphorus pentachloride fume is a severe irritant of the eyes and mucous membranes. Exposure of mice to 120 ppm for 10 minutes was fatal. In humans, the fume causes irritation of the eyes and respiratory tract, and cases of bronchitis have resulted from exposure; although not reported, delayed onset of pulmonary edema may occur. The material on the skin could be expected to cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 167 C (333 F) (sublimes)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of phos-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

phorus pentachloride): Not applicable (reacts rapidly with water in air)

5. Melting point: 167 C (333F) (sublimes)

6. Vapor pressure at 20 C (68 F): Less than 1

7. Solubility in water, g/100 g water at 20 C (68 F): Reacts to form hydrogen chloride and phosphoric acid

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: High temperatures may cause containers to burst. Exposure to moisture will cause the development of pressure in closed containers.

2. Incompatibilities: Contact with water will cause violent spattering and formation of toxic hydrogen chloride gas and phosphoric acid mist. Phosphorus pentachloride reacts with magnesium oxide, chemically active metals such as sodium and potassium, and with alkalies.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosphoric acid mist, and carbon monoxide) may be released in a fire involving phosphorus pentachloride.

4. Special precautions: Phosphorus pentachloride will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: Patty states that phosphorus pentachloride "has a pungent, unpleasant odor." No quantitative information is available concerning the odor threshold, however.

2. Irritation Levels: Patty states that the "vapor or fume is very irritant to all mucous membranes, including the lungs." No quantitative information is available concerning the threshold of eye irritation, however.

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 phosphorus pentachloride 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 phosphorus pentachloride or liquids containing phosphorus pentachloride.

• If employees' clothing may have become contaminated with solid phosphorus pentachloride, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where there is any possibility of exposure of an employee's body to phosphorus pentachloride or liquids containing phosphorus pentachloride, 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 phosphorus pentachloride should be removed immediately and not reworn until the phosphorus pentachloride 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 phosphorus pentachloride or liquids containing phosphorus pentachloride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to phosphorus pentachloride or liquids

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

SANITATION

• Skin that becomes contaminated with phosphorus pentachloride should be immediately washed or showered to remove any phosphorus pentachloride.
• Eating and smoking should not be permitted in areas where solid phosphorus pentachloride is handled, processed, or stored.
• Employees who handle phosphorus pentachloride or liquids containing phosphorus pentachloride 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 phosphorus pentachloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chlorinating agent in organic synthesis or chemical reactant for aryl or alkyl acids and salts, ketones, aldehydes, and synthesis of phosphorus compounds	Local exhaust ventilation; personal protective equipment
Use as a catalyst in organic synthesis in production of polyethylene from ethylene	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 phosphorus pentachloride or liquids containing phosphorus pentachloride 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 phosphorus pentachloride or liquids containing phosphorus pentachloride get on the skin, immediately flush the contaminated skin with water. If phosphorus pentachloride or liquids containing phosphorus pentachloride penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention.

• **Breathing**

If a person breathes in large amounts of phosphorus pentachloride, 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 phosphorus pentachloride or liquids containing phosphorus pentachloride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the phosphorus pentachloride. 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 phosphorus pentachloride 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, or
3. Cover with sodium bicarbonate or an equal mixture of soda ash and slaked lime, dilute carefully with small spray of water, then excess water, and dispose in a secured sanitary landfill.
• Waste disposal method:
See 2 and 3 above.

REFERENCES

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

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 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/or gases and particulates. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Phosphorus Pentasulfide

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: P_2S_5 or P_4S_{10}
- Synonyms: Phosphorus persulfide; regular phosphorus pentasulfide; reactive phosphorus pentasulfide; distilled phosphorus pentasulfide; undistilled phosphorus pentasulfide
- Appearance and odor: Greenish-yellow solid with the odor of rotten eggs.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus pentasulfide 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: Phosphorus pentasulfide on contact with water (including the water normally found in air) may produce hydrogen sulfide. This is a primary health hazard associated with phosphorus pentasulfide. Hydrogen sulfide is a very dangerous chemical. It smells like rotten eggs, but at high concentrations paralyzes the sense of smell so that the odor will not be noticed. Hydrogen sulfide acts as an irritant to the eyes and respiratory tract and can produce severe breathing difficulties which may not occur until a number of hours after exposure has ceased. High concentrations of hydrogen sulfide can stop breathing immediately and cause death. Phosphorus pentasulfide, if allowed to remain on the skin, may cause irritation. On contact with the eyes, it may cause serious irritation which may be delayed for a matter of hours.

2. Long-term Exposure: Repeated exposure to hydrogen sulfide released from contact of water with phosphorus pentasulfide will increase a person's sensitivity to hydrogen sulfide so that irritation of the eyes, coughing, dizziness, headache, and tiredness and other systemic effects may occur more readily.

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 phosphorus pentasulfide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus pentasulfide 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, central nervous system, eyes, and skin should be stressed.

—14" x 17" chest roentgenogram: Phosphorus pentasulfide in contact with water will release hydrogen sulfide, which causes respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Phosphorus pentasulfide in contact with water will release hydrogen sulfide, which causes respiratory impairment. 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

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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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National Institute for Occupational Safety and Health

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

September 1978

indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

• **Summary of toxicology**

Phosphorus pentasulfide dust irritates the eyes and skin. Since it is readily converted in the presence of moisture to hydrogen sulfide gas and phosphoric acid, its inhalation toxicology is based on hydrogen sulfide. The latter is a rapidly acting systemic poison which causes respiratory paralysis with consequent asphyxia at high concentrations; it is an irritant of 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 1 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 may cause pulmonary edema. Prolonged exposure to concentrations 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: 222.3 (or 444.6)
2. Boiling point (760 mm Hg): 513 C (955 F)
3. Specific gravity (water = 1): Bulk density powder = 1.3; solid = 2.1; liquid = 1.7
4. Vapor density (air = 1 at boiling point of phosphorus pentasulfide): Not applicable
5. Melting point: 275 C (527 F)
6. Vapor pressure at 300 C (572 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts to form hydrogen sulfide and liberate heat
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Heat, particularly in presence of moisture or moist air
2. Incompatibilities: Contact with water, alcohols, and strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, hydrogen sulfide, phosphorus pentoxide, phosphoric acid fume, and carbon monoxide) may be released in a fire involving phosphorus pentasulfide.
4. Special precautions: None listed

• **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: 260– 290 C (500– 544 F) (dust); 275 C (527 F) (liquid) (approximately)
3. Minimum explosive concentration: Data not available
4. Extinguishant: Dry chemical, carbon dioxide, dry sand for small fires

• **Warning properties**

1. Odor Threshold: The MCA states that phosphorus pentasulfide reacts with moisture to liberate hydrogen sulfide. Phosphorus pentasulfide, according to the MCA, has a "characteristic hydrogen sulfide odor."
2. Eye Irritation Level: Phosphorus pentasulfide itself is not a known eye irritant. Hydrogen sulfide, however, which is liberated when the compound comes into contact with atmospheric moisture, is known to produce eye (and respiratory) irritation after 1 hour at 50 to 100 ppm (MCA).
3. Evaluation of Warning Properties: Since hydrogen sulfide "paralyzes" olfactory nerves at high concentrations "and, therefore, cannot be detected by odor," phosphorus pentasulfide 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 phosphorus pentasulfide 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 repeated or prolonged skin contact with phosphorus pentasulfide or liquids containing phosphorus pentasulfide.

• If employees' clothing may have become contaminated with solid phosphorus pentasulfide, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with phosphorus pentasulfide should be removed promptly and not reworn until the phosphorus pentasulfide is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where phosphorus pentasulfide or liquids containing phosphorus pentasulfide may contact the eyes.

SANITATION

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

• Eating and smoking should not be permitted in areas where solid phosphorus pentasulfide is handled, processed, or stored.

• Employees who handle phosphorus pentasulfide or liquids containing phosphorus pentasulfide 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 phosphorus pentasulfide may occur and control methods which may be effective in each case:

Operation	Controls
Use in preparation of lubrication oil additives for low-lead gas and reduction of air pollution	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 phosphorus pentasulfide or liquids containing phosphorus pentasulfide 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 phosphorus pentasulfide gets on the skin, dust it off immediately and then flush the contaminated skin with water. If phosphorus pentasulfide or liquids containing phosphorus pentasulfide penetrate through the clothing, remove the clothing promptly and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of phosphorus pentasulfide, 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 phosphorus pentasulfide or liquids containing phosphorus pentasulfide 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 phosphorus pentasulfide 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, or

3. Cover with sodium bicarbonate or an equal mixture of soda ash and slaked lime, dilute carefully with small spray of water, then excess water, and dispose in a secured sanitary landfill.

• Waste disposal methods:

Phosphorus pentasulfide may be disposed of:

1. By making packages of phosphorus pentasulfide in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving phosphorus pentasulfide in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. See 2 and 3 above.

REFERENCES

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

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RESPIRATORY PROTECTION FOR PHOSPHORUS PENTASULFIDE

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate 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.
750 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 750 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 hydrogen sulfide and particulates. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Phosphorus Trichloride

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: PCl_3
- Synonyms: Phosphorus chloride
- Appearance and odor: Colorless to yellow fuming liquid with an odor like hydrochloric acid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphorus trichloride is 0.5 part of phosphorus trichloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3 milligrams of phosphorus trichloride 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 phosphorus trichloride from 0.5 ppm to 0.2 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phosphorus trichloride 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: Phosphorus trichloride is a severe irritant of the eyes, mucous membranes, and skin and may produce severe burns. Inhalation of the vapor may cause irritation of the respiratory tract. It may produce severe breathing difficulties which may be delayed as much as a day in onset. Phosphorus trichloride on contact with the eyes may produce severe burns with permanent eye damage. Swallowing phosphorus trichloride may produce burns of the mouth, throat, and stomach.

2. Long-term Exposure: Repeated inhalation of phosphorus trichloride may cause chronic cough and wheezing.

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 phosphorus trichloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphorus trichloride 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, eyes, and kidneys should be stressed.

—14" x 17" chest roentgenogram: Phosphorus trichloride causes lung damage in humans. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Phosphorus trichloride causes delayed pulmonary edema. 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**

Phosphorus trichloride vapor is a severe irritant of the eyes, mucous membranes, and skin. These effects result primarily from the action of the strong acids, hydrochloric acid and acids of phosphorus, formed with water. In rats, the LC50 was 104 ppm for 4 hours; at autopsy, the chief finding was nephrosis; pulmonary

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 was negligible. Inhalation by humans could be expected to cause injury ranging from mild bronchial spasm to severe pulmonary edema; the onset of severe respiratory symptoms may be delayed for 2 to 6 hours, and after moderate exposure the onset may not occur until 12 to 24 hours later. Prolonged or repeated exposure to low concentrations may induce chronic cough and wheezing; pulmonary changes are non-fibrotic and non-progressive. Phosphorus trichloride causes severe burns in contact with the eyes, skin, or mucous membranes. Although ingestion is unlikely to occur in industrial use, it will cause burns of the mouth, throat, esophagus, and stomach.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 137.4
2. Boiling point (760 mm Hg): 75.9 C (168 F)
3. Specific gravity (water = 1): 1.57
4. Vapor density (air = 1 at boiling point of phosphorus trichloride): 4.75
5. Melting point: −112 C (−169 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): Reacts violently to form hydrogen chloride
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat may cause containers to burst. Containers may burst if water enters them.
2. Incompatibilities: Contact with water or alcohol may cause fires and explosions, particularly when in contact with combustible organic matter. Phosphorus trichloride reacts with chemically active metals such as sodium, potassium, and aluminum or with strong nitric acid.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosphine, diphosphine, phosphoric acid, and carbon monoxide) may be released when phosphorus trichloride decomposes.
4. Special precautions: Phosphorus trichloride will attack some forms of plastics, rubber, and coatings. In the presence of moisture, phosphorus trichloride will severely corrode most metals.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold. The MCA notes that this substance has a pungent odor.
2. Eye Irritation Level: Grant states that "experimentally in cats a concentration of 2 to 4 ppm in air in the course of 6 hours has caused conjunctivitis."
3. Other Information: Grant points out that the vapors are irritating to the respiratory tract also. The *Documentation of TLV's* states that a concentration of 0.7 ppm "was somewhat irritating to animals."
4. Evaluation of Warning Properties: Since phosphorus trichloride causes irritation at only 0.7 ppm, 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**

At the time of publication of this guideline, no measurement method for phosphorus trichloride had been published by NIOSH.

- **Method**

An analytical method for phosphorus trichloride 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

can be discarded or until provision is made for the removal of phosphorus trichloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphorus trichloride, the person performing the operation should be informed of phosphorus trichloride's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid phosphorus trichloride, 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 phosphorus trichloride should be removed immediately and not reworn until the phosphorus trichloride 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 phosphorus trichloride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid phosphorus trichloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use during synthesis of plasticizers and intermediates; and production of intermediates and during chemical synthesis of dyes, pharmaceuticals, other chlorinating agents, and other organic chemicals	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of pesticide intermediates and surfactants	Process enclosure; local exhaust ventilation; personal protective equipment
Use during deposition of metallic coatings; use in treatment of polypropylene before drying in manufacture of knitted fabrics	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 phosphorus trichloride or strong concentrations of phosphorus trichloride 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 phosphorus trichloride gets on the skin, immediately flush the contaminated skin with water. If liquid phosphorus trichloride 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 phosphorus trichloride, 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 phosphorus trichloride has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the phosphorus trichloride. 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 liquid phosphorus trichloride 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, or;
3. Cover with sodium bicarbonate or an equal mixture of soda ash and slaked lime, dilute carefully with a small spray of water, then excess water, and dispose in a secured sanitary landfill.

• Waste disposal method:

Phosphorus trichloride may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill or as in 3 above.

REFERENCES

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

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RESPIRATORY PROTECTION FOR PHOSPHORUS TRICHLORIDE

Condition	Minimum Respiratory Protection* Required Above 0.5 ppm
Vapor Concentration	
25 ppm or less	Any chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxidizable sorbents and providing protection against phosphorus trichloride. A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against phosphorus trichloride Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 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 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 phosphorus trichloride. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Phthalic 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: $C_6H_4(CO)_2O$
- Synonyms: PAN
- Appearance and odor: White solid with a characteristic choking odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phthalic anhydride is 2 parts of phthalic anhydride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 12 milligrams of phthalic anhydride per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for phthalic anhydride a Threshold Limit Value of 1 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Phthalic 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: Phthalic anhydride causes irritation of the eyes, nose, throat, and skin. The irritant effects are worse on moist surfaces. If phthalic anhydride is held in contact with the skin as under clothes or shoes, skin burns may occur. Inhalation of the dust or vapors may cause coughing, sneezing, or nosebleeds. Inhalation may cause attacks of asthma in persons who have previously had asthma.

2. Long-term Exposure: Repeated or prolonged exposure to phthalic anhydride may cause a skin rash or chronic eye irritation. Repeated exposures may also cause an allergic type of skin rash. It may cause bronchitis and asthma.

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 phthalic anhydride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phthalic 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 phthalic anhydride would be expected to be at increased risk from exposure. Examination of the eyes, respiratory tract, 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**

Phthalic anhydride in the form of vapor, fume, or dust irritates the eyes; it is both an irritant and sensitizer of the skin and respiratory tract, and may produce asthma on repeated exposure. Cats repeatedly exposed to 3700 mg/m³ became drowsy, lost appetite and vomited; liver and kidney injury occurred. In workers, air concentrations of 30 mg/m³ caused conjunctivitis; at 25 mg/m³ there were signs of mucous membrane irritation. Workers exposed to undetermined concentrations of mixed vapors of phthalic acid and phthalic anhydride developed conjunctivitis, bloody nasal discharge, atrophy of the nasal mucosa, hoarseness, cough, occasional bloody

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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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sputum, and bronchitis. A report of emphysema among workers exposed to phthalic anhydride is questionable. Several cases of bronchial asthma resulted; there was skin sensitization with occasional urticaria and eczematous response. Phthalic anhydride is a direct but delayed irritant of the skin; it is more severely irritating in contact with water, due to the pronounced effects of the phthalic acid which is formed. Prolonged or repeated exposure also may cause dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 148
  2. Boiling point (760 mm Hg): 284 C (543 F)
  3. Specific gravity (water = 1): 1.5
  4. Vapor density (air = 1 at boiling point of phthalic anhydride): 5.1
  5. Melting point: 131 C (268 F)
  6. Vapor pressure at 20 C (68 F): Less than 0.05 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.62 (reacts slowly)
  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 phthalic acid fumes and carbon monoxide) may be released in a fire involving phthalic anhydride.
  4. Special precautions: Liquid phthalic anhydride will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 151 C (304 F) (closed cup)
  2. Autoignition temperature: 570 C (1058 F)
  3. Flammable limits in air, % by volume (at elevated temperatures): Lower: 1.7; Upper: 10.4
  4. Minimum explosive dust concentration: 0.015 g/l
  5. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**

According to both Patty and the *Hygienic Guide*, exposure to a concentration of 30 mg/m^3 causes "definite conjunctival irritation." This concentration is not stated specifically to be the threshold of eye irritation, 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 phthalic anhydride on a cellulose membrane filter, followed by treatment with aqueous ammonia, hydrolysis, and anlysis with a high-performance liquid chromatograph. An analytical method for phthalic anhydride 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 phthalic anhydride or liquids containing phthalic anhydride.
- If employees' clothing may have become contaminated with solid phthalic anhydride, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with phthalic anhydride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of phthalic anhydride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phthalic anhydride, the person performing the operation should be informed of phthalic anhydride's hazardous properties.

• Non-impervious clothing which becomes contaminated with phthalic anhydride should be removed immediately and not reworn until the phthalic anhydride is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid phthalic anhydride or liquids containing phthalic anhydride may contact the eyes.

SANITATION

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

• Employees who handle solid phthalic anhydride or liquids containing phthalic 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 phthalic anhydride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of plasticizers for use in polyvinyl chloride, polyvinyl acetate, copolymer resins, cellulosic plastics, alkyd resins, and nondrying oils or natural resins to enhance properties; manufacture of unsaturated polyester resins for use in structural building parts, swimming pools, automotive parts, and luggage	Process enclosure; general dilution ventilation
Use in synthesis of dyes; use in manufacture of chemicals and chemical intermediates for production of insecticides, insect repellants, chemical reagents, urethane polymers, perfumes, and weed killers	Process enclosure; general dilution ventilation; personal protective equipment
Use in manufacture of pharmaceuticals and pharmaceutical intermediates; manufacture of metallic and acid salts; manufacture of epoxy resins as curing and hardening agents	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of fire retardants for use as components of polyester resins	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 phthalic anhydride 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 solid phthalic anhydride or liquids containing phthalic anhydride get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid phthalic anhydride or liquids containing phthalic 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 phthalic 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 phthalic 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 phthalic 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. Liquid containing phthalic anhydride should be absorbed in vermiculite, dry sand, earth, or a similar material for disposal in a secured sanitary landfill.

• Waste disposal methods:

Phthalic anhydride may be disposed of:

1. By making packages of phthalic 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 phthalic anhydride in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. Liquid containing phthalic anhydride should be absorbed in vermiculite, dry sand, earth, or a similar material and deposited in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR PHTHALIC ANHYDRIDE

Condition	Minimum Respiratory Protection* Required Above 2 ppm
Particulate or Vapor Concentration	
100 ppm or 600 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.
1670 ppm or 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 1670 ppm or 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 Picric 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: $HOC_6H_2(NO_2)_3$
- Synonyms: 2,4,6-Trinitrophenol; lyddite; pertite; shimose; melinite
- Appearance and odor: Odorless yellow solid or paste.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for picric acid is 0.1 milligram of picric acid per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Effects of overexposure**

Exposure to picric acid dust and fume may cause eye and skin irritation. The dust and solutions of picric acid may cause an allergic skin rash. The skin and hair may be stained yellow. Inhalation of high concentrations of dust has caused unconsciousness, weakness, muscle pain, and kidney problems. Swallowing picric acid may cause a bitter taste, headache, dizziness, nausea, vomiting, and diarrhea. High doses may cause destruction of the red blood cells and damage to the kidneys and liver with blood in the urine. High doses such as these may color the skin and other tissues yellow and cause yellow tinted vision.

- **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 picric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to picric 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. Persons with a history of asthma, allergies, or known sensitization to picric acid may be at increased risk from exposure. Examination of the kidneys, liver, and blood should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to picric acid, 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 picric acid, 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**

Picric acid dust causes sensitization dermatitis. This usually occurs on the face, especially around the mouth and the sides of the nose; the condition progresses from edema, through the formation of papules and vesicles, to ultimate desquamation. The skin and hair of workers handling picric acid are stained yellow. Inhalation of high concentrations of the dust by one worker caused temporary coma followed by weakness, myalgia, anuria, and later polyuria. Following ingestion of 2 to 5 g of picric acid, which has a bitter taste, there may 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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headache, vertigo, nausea, vomiting, diarrhea, yellow coloration of the skin, hematuria, and albuminuria; high doses cause destruction of erythrocytes, hemorrhagic nephritis, and hepatitis. High doses which cause systemic intoxication will color all tissues yellow, including the conjunctiva and aqueous humor, and cause apparent yellow-tinted vision. Corneal injury has resulted from a splash of a solution of picric acid into the eyes; dust or fume may cause eye irritation which may be aggravated by sensitization.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 229.1
2. Boiling point (760 mm Hg): Greater than 300 C (572 F); explodes
3. Specific gravity (water = 1): 1.6— 1.76
4. Vapor density (air = 1 at boiling point of picric acid): Not applicable
5. Melting point: 122 C (252 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): 1.4
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Explodes above 300 C (572 F)
2. Incompatibilities: Contact with copper, lead, zinc, and other metals (or with their salts) can form salts of picric acid that are initiators and much more sensitive to shock than picric acid itself. Shock-sensitive salts also include ammonium salts and calcium salts; the calcium salt may form when picric acid comes into contact with plaster or concrete.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving picric acid.
4. Special precautions: Protect from shock.

- **Flammability**

1. Flash point: 150 C (302 F) (closed cup)
2. Autoignition temperature: 300 C (572 F) (approx).
3. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): 82 cm
4. Explosion temperature (temperature required to cause explosion in 5 seconds): 322 C (612 F)
5. Flammable limits in air, % by volume: Data not available
6. Extinguishant: Water. Do not attempt to extinguish massive fires.

- **Warning properties**

The ILO states, "The effects of picric acid on the eyes include irritation, corneal injury and strange visual effects, e.g. yellow appearance of objects, and yellow colouring of the tissues." Grant also states that "picric acid dust or fumes cause irritation of the eyes of men and animals, and this may be aggravated by sensitization." No quantitative information is available concerning the air concentrations which produce these effects, however. Information is not available concerning the threshold of 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 vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure picric acid may be used. An analytical method for picric acid 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 solid picric acid or liquids containing picric acid, where skin contact may occur.

- If employees' clothing may have become contaminated with picric acid, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which may have become contaminated with picric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of picric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the picric acid, the person performing the operation should be informed of picric acid's hazardous properties.
- Non-impervious clothing which becomes contaminated with picric acid should be removed promptly and not reworn until the picric acid is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid picric acid or liquids containing picric acid may contact the eyes.

SANITATION

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

Operation	Controls
Use in munitions and explosives manufacturing	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of dyes and dye intermediates in textile industry; use in manufacture of medicinals; use in etching of metal on printing plates of copper, steel, or other metals	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of pyrotechnics and compounds for pyrotechnics as color intensifiers and as an oxidizer in matches	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use as a chemical reagent in identification, isolation, and purification of other compounds; use in manufacture of colored glass; and in the manufacture of electric batteries	Material substitution; 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 picric acid or liquids containing picric acid 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 picric acid or liquids containing picric acid get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If picric acid or liquids containing picric acid penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of picric 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 picric acid or liquids containing picric acid 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 picric acid is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. Attempt to reclaim spilled material; however, do not sweep or burn unless this is supervised by explosive experts.

• Waste disposal method:

Picric acid may be disposed of only by explosives experts.

ADDITIONAL INFORMATION

To find additional information on picric acid, look up picric acid 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 PICRIC ACID

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
1 mg/m³ or less	Any dust and mist respirator, except single-use respirator or quarter-mask.** Any fume respirator or high efficiency particulate filter respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a 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 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 dust and mist 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 Pival

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: $C_{14}H_{14}O_3$
- Synonyms: 2-Pivalyl-1,3-indandione; pivalyl; tert-butyl-valone; 2-pivaloyl-1,3-indandione; 1,3-dioxo-2-pivaloy-lindane; pindone
- Appearance and odor: The technical material, which is a 0.5% concentrate in an inert solid, is a bright yellow solid with almost no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Pival is 0.1 milligram of Pival per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pival may be absorbed by swallowing, or indirectly by inhalation, and is probably not significantly absorbed through the skin.

- **Effects of overexposure**

Pival causes no immediate symptoms. Swallowing Pival, particularly in repeated smaller doses, may cause generalized bleeding, such as nose bleeds, excessive bleeding of minor cuts, smoky urine, or black, tarry stools. A person may experience stomach and back pain one to several days after being exposed to Pival.

- **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 Pival.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Pival at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination, including a complete blood count: The effects of overexposure from Pival can be enhanced or mimicked in individuals who have blood disorders with bleeding tendencies or with diseases that cause internal bleeding, such as peptic ulcer. Also, those with chronic liver disease may be increased risk, as are those on therapeutic doses of anticoagulants.

—Prothrombin time: The principal action of Pival is to reduce the level of prothrombin, prolonging the prothrombin time. This test is critical to the monitoring of exposed employees.

2. Periodic Medical Examination: At three months from the first exposure and annually thereafter, the employer should make available to the employee medical procedures listed under the preplacement examination. Also, if an employee develops signs or symptoms associated with Pival exposure at any time during employment, the employer should provide medical examinations to the employee.

- **Summary of toxicology**

Pival is a vitamin K antagonist, inhibiting prothrombin formation. Since repeated doses have a cumulative effect, a toxic concentration may be reached after several days of exposure to small doses. In rats, the ingestion of a single large dose of Pival causes rapid death due to pulmonary and visceral congestion without hemorrhage and may not be related to vitamin K antagonism. Death in animals from chronic exposure is due to multiple internal hemorrhage.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 230
2. Boiling point (760 mm Hg): Data not available

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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3. Specific gravity (water = 1): 1.06
4. Vapor density (air = 1 at boiling point of Pival): Data not available
5. Melting point: 110 C (230 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): 0.0018
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Very high temperatures
2. Incompatibilities: None known
3. Hazardous decomposition products: None known
4. Special precautions: None known

• **Flammability**

1. Not flammable

• **Warning properties**

Pival 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 sampies 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 Pival 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

• If employees' clothing may have become contaminated with Pival, employees should change into uncontaminated clothing before leaving the work premises.

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

SANITATION

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

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

Operation	Controls
Liberation during mixing and packaging operations in pesticide formulations	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area
Liberation during mixing and blending of pesticide formulation with other materials (cereal bait, liquid, etc).	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area
Liberation during synthesis of substance; during use as an intermediate in pharmaceutical synthesis	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area
Liberation during container reclamation, process clean-up, etc.	Local exhaust ventilation; respiratory protective equipment; separation of food storage and eating area from work area

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 Pival 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.

• **Swallowing**

When Pival 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 Pival 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:

Pival may be disposed of:

1. By making packages of Pival in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving Pival 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 PIVAL

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use respirators.
1 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.
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. Any high efficiency particulate filter respirator with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use respirators. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Soluble Platinum Salts (as Platinum)

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 platinum salts (as platinum). Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Sodium chloroplatinate

- Formula: Na_2PtCl_6-$6H_2O$
- Synonyms: None
- Appearance and odor: Yellow-orange, odorless solid.

Ammonium chloroplatinate

- Formula: $(NH_4)_2PtCl_6$
- Synonyms: Ammonium hexachloroplatinate
- Appearance: Yellow-orange solid.

Platinum tetrachloride

- Formula: $PtCl_4$
- Synonyms: Platinum (IV) chloride
- Appearance: Brown-red crystals.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble platinum salts is 0.002 milligram of soluble platinum salts (as platinum) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble platinum salts can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Soluble platinum salts may cause irritation of the eyes, nose, and throat.

2. Long-term Exposure: Repeated exposure to soluble platinum salts may cause both respiratory and skin allergies. The respiratory reaction starts with sneezing and a runny nose. These effects may be followed by chest tightness, shortness of breath, blue discoloration of the skin, and wheezing. The skin reaction consists of an itchy red 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 soluble platinum salts.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble platinum salts 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 soluble platinum salts would be expected to be at increased risk from exposure. Examination of the respiratory 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**

Soluble platinum salts in the form of dusts and sprays cause asthma, skin sensitization, and eye irritation; elemental platinum does not produce these effects.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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National Institute for Occupational Safety and Health

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Occupational Safety and Health Administration

Workers repeatedly exposed to platinum salts in concentrations of from 2 to 20 ug/m^3 of workroom air developed irritation of the nose and upper respiratory tract with sneezing and running of the eyes, leading to cough, chest tightness, asthmatic wheezing with dyspnea and cyanosis, which became progressively more severe with further exposure. A relative lymphocytosis is commonly present. Skin exposure results in contact dermatitis with pruritis and urticaria; an eczematous eruption often results. Some exposed individuals experience both dermal and respiratory effects due to sensitization; the majority of individuals exposed repeatedly to platinum salts develop some allergic symptoms. Removal from platinum salt exposure results in almost immediate relief of asthma; the dermatitis usually clears in 1 to 2 days but may be persistent. In the eyes, the dusts cause a burning sensation, lacrimation, and conjunctival hypermia sometimes associated with photophobia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Sodium chloroplatinate**
  1. Molecular weight: 561.9
  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 platinum salts): Not applicable
  5. Melting point: Loses water at 100 C (212 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 50
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Ammonium chloroplatinate**
  1. Molecular weight: 443.9
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 3.1
  4. Vapor density (air = 1 at boiling point of soluble platinum salts): 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): 0.7
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Platinum tetrachloride**
  1. Molecular weight: 336.9
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 4.3
  4. Vapor density (air = 1 at boiling point of soluble platinum salts): Not applicable
  5. Melting point: Decomposes at 370 C (698 F)
  6. Vapor pressure at 20 C (68 F): Not applicable
  7. Solubility in water, g/100 g water at 25 C (77 F): 58.7
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: High temperatures may cause formation of poisonous chlorine gas.
  2. Incompatibilities: None
  3. Hazardous decomposition products: Toxic gases and vapors (such as chlorine) may be released when chlorine-containing soluble platinum salts decompose.
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Grant reports that "the dusts of soluble platinum salts cause a burning sensation in the eyes, lacrimation, and conjunctival hyperemia, sometimes associated with photophobia, which suggests that the corneal epithelium may be involved." However, no quantitative information concerning the concentrations of the dusts which produce these symptoms is given.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of soluble platinum salts on a filter, followed by treatment with nitric and perchloric acids, solution in acid, and atomic absorption analysis. An analytical method for soluble platinum salts 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).
(order number PB 265 029).

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 repeated or prolonged skin contact with soluble platinum salts or liquids containing soluble platinum salts, where skin contact may occur.

• If employees' clothing may have become contaminated with soluble platinum salts or liquids containing soluble platinum salts, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with soluble platinum salts should be removed promptly and not reworn until the soluble platinum salts are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble platinum salts or liquids containing soluble platinum salts may contact the eyes.

SANITATION

• Skin that becomes contaminated with soluble platinum salts should be promptly washed or showered to remove any soluble platinum salts.

• Eating and smoking should not be permitted in areas where soluble platinum salts or liquids containing soluble platinum salts are handled, processed, or stored.

• Employees who handle soluble platinum salts or liquids containing soluble platinum salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as catalysts in production of high octane gasoline; nitric and sulfuric acids; vinyl esters, petrochemicals, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use and re-use in reclamation of platinum ore; use in electroplating industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in photographic and related industries as a photographic paper sensitizer	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 soluble platinum salts or liquids containing soluble platinum salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

• **Skin Exposure**

If soluble platinum salts or liquids containing soluble platinum salts get on the skin, promptly flush the contaminated skin with water. If soluble platinum salts or liquids containing soluble platinum salts penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of soluble platinum salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When soluble platinum salts or liquids containing soluble platinum salts have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Under-

stand 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 platinum salts or liquids containing soluble platinum salts are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquids containing soluble platinum salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Soluble platinum salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR SOLUBLE PLATINUM SALTS (AS PLATINUM)

Condition	Minimum Respiratory Protection* Required Above 0.002 mg/m³
Particulate Concentration	
0.1 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.
2 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
4 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 4 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR PORTLAND CEMENT

INTRODUCTION

This guideline summarizes pertinent information about Portland cement (containing less than 1 percent quartz) 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**

  Varies with composition of specific cement

- **Synonyms**

  Hydraulic cement, Portland cement silicate, cement

- **Identifiers**

  1. CAS No.: 65997-15-1
  2. RTECS No.: VV8770000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  Portland cement is a finely divided gray powder containing less than 1 percent silica and composed of lime, alumina, silica, and iron oxide; small amounts of magnesia, sodium, potassium, and sulfur are also present. This substance is odorless.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: Varies with specific cement
  2. Boiling point: Not applicable
  3. Specific gravity: Not reported
  4. Vapor density: Not applicable
  5. Melting point: Not applicable
  6. Vapor pressure at 20°C (68°F): Not applicable
  7. Solubility: Insoluble in water
  8. Evaporation rate: Not applicable

- **Reactivity**

  1. Conditions contributing to instability: None reported
  2. Incompatibilities: None reported
  3. Hazardous decomposition products: None reported
  4. Special precautions: None reported.

- **Flammability**

  The National Fire Protection Association has not

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assigned a fire hazard rating for Portland cement; 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 Portland cement 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 Portland cement.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for Portland cement is 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable fraction) as 8-hour 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/m3 (respirable fraction) as TWAs for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned Portland cement a threshold limit value (TLV) of 10 mg/m3 (total dust) 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 physical irritation associated with exposure to Portland cement [NIOSH 1992; ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

1. *Effects on Animals:* Instilled intratracheally, cement dust caused an absorptive reaction in guinea pig lungs. Peritoneal nodules formed initially and then decreased progressively in size and eventually resolved spontaneously [ACGIH 1991].

2. *Effects on Humans:* Portland cement dust causes eye irritation, and prolonged or repeated contact of the dust or cement with the skin causes dermatitis [Hathaway et al. 1991]. Fifteen of 95 cement workers studied had a mild dermatitis of the hands [Hathaway et al. 1991]. A study of 2,736 Portland cement workers revealed that 5.4 percent of these workers had dyspnea, compared with a 2.7 percent prevalence among controls. There were no differences in mean pulmonary function test results between the two groups [Hathaway et al. 1991]. The mean cement dust exposure for these workers was 0.57 mg/m^3 (respirable dust), with peaks to 46 mg/m3 [Hathaway et al. 1991].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to Portland cement include physical irritation of the eyes, with redness and tearing; coughing; and redness, roughness, and scaling of the skin.

2. *Chronic exposure:* The signs and symptoms of repeated or prolonged exposure of the skin to Portland cement include coughing, expectoration, exertional dyspnea, and skin redness, blistering, burns, and, in some individuals, raised itching areas characteristic of hives.

- **Emergency procedures**

WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of irritation!

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

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

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

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose, or use a soft tissue to remove particulates or residues from the nostrils.

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

4. *Ingestion exposure:* Seek medical attention and take the following steps if a large amount of Portland cement is ingested:

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

   —Have the victim drink a fluid such as water.

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

—Use as a binding agent in concrete and mortar

The following methods are effective in controlling worker exposures to Portland cement, 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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MEDICAL MONITORING

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

- **Preplacement medical evaluation**

  Before a worker is placed in a job with a potential for

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

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

Periodic medical examinations and biological monitoring

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

- **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 Portland cement is made using a tared low ash polyvinyl chloride (LAPVC) filter, 5 microns, preceded by a 10-mm nylon cyclone. A maximum air volume of 960 liters is collected at a maximum flow rate of 2 liters/min. A gravimetric analysis is then performed to measure compliance with the respirable Portland cement standard. Following this determination, an x-ray diffraction analysis of respirable quartz is done to determine compliance with the quartz standard. These methods are described in the *OSHA Industrial Hygiene Technical Manual* [OSHA 1985a], *NIOSH Occupational Exposure Sampling Strategy Manual* [NIOSH 1977] and Method No. ID-142 of the *OSHA Analytical Methods Manual* [OSHA 1985b].

PERSONAL HYGIENE

If Portland cement dust contacts the skin, workers should flush the affected areas immediately with plenty of water, and then wash with soap and water.

Clothing contaminated with Portland cement dust should be removed, 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 Portland cement, particularly its potential to cause dermatitis on prolonged contact.

A worker who handles Portland cement 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 Portland cement is handled, processed, or stored.

STORAGE

Portland cement 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 Portland cement should be protected from physical damage.

SPILLS

In the event of a spill involving Portland cement, 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. Avoid creating dust during cleanup by using a vacuum or a wet method for cleanup.
4. For dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

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

- **Emergency planning requirements**

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

- **Reportable quantity requirements for hazardous releases**

  Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.30] to notify the National Response Center of an accidental release of Portland cement; 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 Portland cement 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 Portland cement 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 Portland cement 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* [1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, and gauntlets) should be worn to prevent prolonged skin contact with Portland cement. 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 Portland cement 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 Portland cement.

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

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Occupational Health Guideline for 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.

APPLICABILITY

The general guidelines contained in this document apply to all cyanides. Physical and chemical properties of two specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Potassium cyanide

- Formula: KCN
- Synonyms: None
- Appearance and odor: White solid with a faint almond odor.

Sodium cyanide

- Formula: NaCN
- Synonyms: None
- Appearance and odor: White solid with a faint almond odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyanide is 5 milligrams of cyanide 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 a ceiling of 5 milligrams cyanide per cubic meter of air 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**

Cyanide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. Sufficient cyanide may be absorbed through the skin, especially if there are cuts to cause fatal poisoning.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation or ingestion of cyanide salts may be rapidly fatal. Larger doses by inhalation or swallowing may cause the person to rapidly lose consciousness, stop breathing, and die. In some cases, there are convulsions. At lower levels of exposure, the earlier symptoms include weakness, headache, confusion, nausea, and vomiting. These symptoms may be followed by unconsciousness and death. Occasionally, convulsions occur. Milder forms of intoxication may result only in weakness, dizziness, headache, and nausea. The dust of cyanide salts is irritating to the eyes. In the presence of tears, it may cause the symptoms of poisoning described above. The dust of cyanide salts may produce irritation of the nose and skin. Strong solutions of cyanide salts are corrosive and may produce ulcers.

2. Long-term Exposure: Effects from chronic exposure to 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 cyanide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 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,

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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 those 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. The skin should be examined for evidence of chronic disorders.

—Skin disease: Cyanide 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: Cyanide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Cyanide 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.

3. First Aid Kits: First aid kits should be readily available in workplaces where there is a potential for the release of 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 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**

The dust of cyanide salts, 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. In the presence of even weak acids, hydrocyanic acid (HCN) gas is liberated from cyanide salts; a few inhalations of higher 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. The ingestion by humans of 50 to 100 mg of sodium or potassium cyanide may also be fatal. 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 is usually increased initially and at later stages becomes 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. Sodium cyanide dust is irritating to the eyes; in the presence of tears it may liberate HCN, which can be absorbed and cause systemic intoxication. Skin contact with dust may be irritating; strong solutions on the skin produce ulcers which are slow in healing. Cyanide is one of the few toxic materials for which an antidote exists; 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—Potassium cyanide**

1. Molecular weight: 65.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.55
4. Vapor density (air = 1 at boiling point of potassium cyanide): Not applicable
5. Melting point: 635 C (1175 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 71.6
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium cyanide**

1. Molecular weight: 49
2. Boiling point (760 mm Hg): 1500 C (2732 F) (extrapolated)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of sodium cyanide): Not applicable
5. Melting point: 560 C (1040 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 58
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None. Hazardous if kept in closed containers. It may form toxic concentrations of hydrogen cyanide gas when in prolonged contact with air in a closed area.

2. Incompatibilities: Contact with strong oxidizers such as nitrates and chlorates may cause fires and

explosions. Contact with acids and acid salts causes immediate formation of toxic and flammable hydrogen cyanide gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide and carbon monoxide) may be released when cyanide decomposes.

4. Special precautions: Cyanide may react with carbon dioxide in ordinary air to form toxic hydrogen cyanide gas.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of sodium or potassium cyanide. HCN, however, is evolved from these substances in the presence of moisture. The Manufacturing Chemists Association states that "although HCN has a characteristic odor, its toxic action at hazardous concentrations is so rapid that it is of no value as a warning property."

2. Eye Irritation Level: Cyanide (as CN) is not known to be an eye irritant. However, according to Grant, HCN can produce eye irritation after chronic exposures.

3. Evaluation of Warning Properties: Although cyanide (as CN) has a negligible vapor pressure, in the presence of moisture HCN can be given off. HCN does not 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 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**

Sampling and analyses may be performed by collection of cyanide with a cellulose membrane filter and an impinger containing sodium hydroxide, followed by analysis by direct potentiometry. An analytical method for cyanide 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 cyanide or liquids containing cyanide.

• If employees' clothing has had any possibility of being contaminated with cyanide, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where there is any possibility of exposure of an employee's body to cyanide or liquids containing cyanide, 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 cyanide should be removed immediately and not reworn until the cyanide 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 cyanide or liquids containing cyanide contacting the eyes.

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

SANITATION

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

Operation	Controls
Use as fumigants and pesticides in greenhouses, ships, mills, and warehouses; use of cyanogen chloride as a warning agent in fumigant gases	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in metal treatment in nitriding, tempering, and case hardening steel; coloring of metals by chemical or electrolytic process; cleaning and coating metals; welding and cutting of heat-resistant metals; liberation during ore extraction and metal purification	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use of calcium cyanamid in fertilizer on soil; during chemical synthesis for manufacture of intermediates in pharmaceuticals, dyes, vitamins, plastics, and sequestering agents; preparation of nitriles, carbylamines, cyano fatty acids, and inorganic cyanides	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in cellulose technology; paper manufacture; in dyeing; as cement stabilizers; use in photography as fixatives, and in blueprinting and process engraving; liberation in blast furance gases or in handling of illuminating gas	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 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 cyanides.

• **Skin Exposure**

If cyanide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If cyanide 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 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 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 AND DISPOSAL PROCEDURES

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

• If cyanide 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 treatment in a cyanide disposal system.

• Waste disposal method:

After treatment as in above, cyanide may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR CYANIDE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
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 hydrogen cyanide and particulates. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Propane

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: $CH_3CH_2CH_3$
- Synonyms: Dimethylmethane
- Appearance and odor: Colorless, odorless gas (a foul-smelling odorant is usually added).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propane is 1000 parts of propane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 1800 milligrams of propane per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propane can affect the body if it is inhaled.

- **Effects of overexposure**

Overexposure to propane may cause dizziness, disorientation, and excitation. Greater exposure may cause unconsciousness and death. Contact with liquefied propane may cause a freezing injury or 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 propane.

- **Recommended medical surveillance**

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

- **Summary of toxicology**

Propane, a gas at ordinary temperatures, is an asphyxiant in very high concentrations. Guinea pigs exposed to concentrations of up to 5.5% propane by volume (55,000 ppm) for 1 to 2 hours showed tremors after 5 minutes, then nausea, retching and stupefaction; all survived and at autopsy had no significant tissue damage. Brief exposures to 10,000 ppm caused no symptoms in human subjects; 100,000 ppm produced slight dizziness in a few minutes of exposure but was not noticeably irritating to the eyes, nose, or respiratory tract. In the very few reports of accidental overexposure, there was disorientation, excitation, excessive salivation, headache, and vomiting. Liquid propane may cause frostbite.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 44.1
2. Boiling point (760 mm Hg): −42.1 C (−43.7 F)
3. Specific gravity (water = 1): 0.5 (liquid)
4. Vapor density (air = 1 at boiling point of propane): 1.6
5. Melting point: −187.7 C (−305.8 F)
6. Vapor pressure at 20 C (68 F): 8.6 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
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 propane.
4. Special precautions: Liquid propane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: Not applicable (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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2. Autoignition temperature: 450 C (842 F)

3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 9.5

4. Extinguishant: Stop flow of gas.

• **Warning properties**

1. Odor Threshold: Patty reports that the odor threshold of propane is 20,000 ppm.

2. Irritation Levels: According to Patty, exposure to concentrations as high as 100,000 ppm "is not noticeably irritating to the eyes, nose, or respiratory tract."

3. Evaluation of Warning Properties: Propane has poor warning properties. The odor threshold is 20 times the permissible exposure limit, and no noticeable irritation is produced at a concentration 100 times the permissible exposure limit.

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 propane may be used. An analytical method for propane 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 propane or from contact with vessels containing liquid propane.

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

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation from use as a component of liquid petroleum gas for commercial and industrial usage	General dilution ventilation
Use as feedstock in cracking process in production of ethylene and propylene and motor gasoline with high antiknock properties and stability	Process enclosure; general dilution ventilation
Use as a basic material in chemical synthesis for oxidation, alkylation, nitration, and chlorination	Process enclosure; general dilution ventilation
Use as a solvent and extractant in de-asphalting and degreasing of crude oils in production of lubricating oils, refining of fish and vegetable oils, extraction of oils from agricultural products, and segregate of specialty oils	Process enclosure; general dilution ventilation

Use as a refrigerant in chemical, petroleum refining, and gas processing operations, low-temperature crystallizers, and helium recovery from natural gas	Process enclosure; general dilution ventilation
Use as a fuel in welding and cutting operations; use in high-grade metallurgical work in which sulfur-free fuel is essential	General dilution ventilation
Use in oil wells to increase production of crude oil	Process enclosure
Use in desalination of water; use in hydrocarbon-fueled cells as source of power (experimental)	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 liquefied propane gets into the eyes, flush eyes immediately with large amounts of water. Do not use hot water for eye flushing. Get medical attention immediately.

- **Skin Exposure**

If liquefied propane gets on the skin, immediately flush the contaminated skin with water. If liquefied propane 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 propane, 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 propane 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:

Propane may be disposed of by burning at a safe location or in a suitable combustion chamber.

REFERENCES

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

RESPIRATORY PROTECTION FOR PROPANE

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 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 escape self-contained breathing apparatus.

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

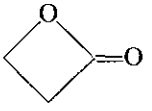
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR beta-PROPIOLACTONE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about beta-propiolactone 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:** $C_3H_4O_2$
- **Structure:**



- **Synonyms:** 2-Oxetanone; BPL; hydracrylic acid beta-lactone; 3-hydroxypropionic acid lactone; propanolide; 1,3-propiolactone; 3-propiolactone; beta-propionolactone.
- **Identifiers:** CAS 57-57-8; RTECS RQ7350000; DOT not assigned
- **Appearance and odor:** Colorless liquid with a pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72.06
2. Boiling point (at 760 mmHg): 162 °C (323.6 °F), decomposes
3. Specific gravity (water = 1): 1.1460
4. Vapor density (air = 1 at boiling point of beta-propiolactone): 2.5
5. Melting point: -33.4 °C (-28.12 °F)
6. Vapor pressure at 25 °C (77 °F): 3.4 mmHg
7. Solubility in water, g/100 g water at 25 °C (77 °F): 37
8. Evaporation rate (butyl acetate = 1): 0.223
9. Saturation concentration in air (approximate) at 25 °C (77 °F): 0.45% (4,473 ppm)

- **Reactivity**

1. Incompatibilities: beta-Propiolactone polymerizes during storage, hydrolyzes readily in water, and decomposes if stored at room temperature.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving beta-propiolactone.
3. Caution: beta-Propiolactone can polymerize and rupture containers, especially at elevated temperatures.

- **Flammability**

1. Flash point: 74 °C (165 °F) (closed cup)
2. Flammable limits in air, % by volume: Lower, 2.9; upper, not available
3. Extinguishant: Dry chemical, alcohol foam, or carbon dioxide
4. Class IIIA Combustible Liquid (29 CFR 1910.106), Flammability Rating 2 (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 beta-propiolactone; however, the OSHA standard requires implementation of stringent controls wherever beta-propiolactone or solid or liquid mixtures containing at least 0.1% by weight or volume of beta-propiolactone 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 1910.1013, beta-Propiolactone. 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-propiolactone as an A2 substance (suspected human carcinogen) having an assigned threshold limit value (TLV®) of 0.5 parts of beta-propiolactone per million parts of air (ppm) [1.5 milligrams per cubic meter of air (mg/m^3)] as a time-weighted average (TWA) concentration for a normal 8-hour workday or a 40-hour workweek.

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HEALTH HAZARD INFORMATION

• **Routes of exposure**
beta-Propiolactone may cause adverse health effects following exposure via inhalation, ingestion, or dermal contact.

• **Summary of toxicology**
Effects on animals: In rats, acute oral administration or intraperitoneal injection of beta-propiolactone caused muscular spasms, respiratory difficulty, convulsions, and death. Acute intravenous injection caused kidney tubule and liver damage. Subcutaneous injection of beta-propiolactone in rats and mice produced cancer at the sites of administration. Single intraperitoneal injections in suckling mice produced lymphatic tumors and liver cancer.

• **Signs and symptoms of exposure**
Short-term (acute): Exposure to beta-propiolactone can cause irritation and blistering of the skin, hair loss, and scarring. Eye contact with liquid beta-propiolactone can cause permanent corneal opacification.

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-propiolactone, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, kidneys and respiratory systems. Medical surveillance for respiratory diseases 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 beta-propiolactone 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 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 beta-propiolactone. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, eyes, liver, 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 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 beta-propiolactone may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

MONITORING AND MEASUREMENT PROCEDURES

• **Method**
There are no NIOSH-validated sampling and analytical methods for beta-propiolactone.

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-propiolactone 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 beta-propiolactone 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 the 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 beta-propiolactone 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-propiolactone from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of beta-propiolactone'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-propiolactone 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 1910.1013:

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

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

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to beta-propiolactone 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 beta-propiolactone

Operations	Controls
During use in the manufacture of acrylic acids and esters; during use in the sterilization of blood plasma, tissue grafts, and surgical instruments; during use in research and laboratory facilities	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 beta-propiolactone, 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 beta-propiolactone, an eye-wash fountain should be provided within the immediate work area for emergency use.

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

If beta-propiolactone gets on the skin, wash it immediately with soap and water. If beta-propiolactone 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 aras of spills or leaks be decontaminated before removing the protective garments and hoods and showering.

If beta-propiolactone 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 beta-propiolactone should be absorbed on paper towels and placed in an appropriate container.
4. Large quantities of liquids containing beta-propiolactone may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing beta-propiolactone 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 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 beta-propiolactone

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 n-Propyl 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: $CH_3COOCH_2CH_2CH_3$
- Synonyms: Propyl acetate; acetic acid n-propyl ester
- Appearance and odor: Colorless liquid with a mild, fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for n-propyl acetate is 200 parts of n-propyl acetate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 840 milligrams of n-propyl acetate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Propyl 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 n-propyl 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 n-propyl acetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to n-propyl 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 n-propyl acetate exposure.

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

—Skin disease: n-Propyl 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 n-propyl 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 n-propyl 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 n-propyl acetate are chiefly irritation of the conjunctiva and upper respiratory tract, followed by narcosis. Cats exposed to 5300 ppm for 6 hours daily showed eye irritation and salivation; at 24,500 ppm there was narcosis and death. 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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U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 102
  2. Boiling point (760 mm Hg): 101.6 C (215 F)
  3. Specific gravity (water = 1): 0.89
  4. Vapor density (air = 1 at boiling point of n-propyl acetate): 3.5
  5. Melting point: −95 C (−140 F)
  6. Vapor pressure at 20 C (68 F): 25 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 2
  8. Evaporation rate (butyl acetate = 1): 2.75
- **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 n-propyl acetate.
  4. Special precautions: n-Propyl acetate will dissolve many plastics and resins.
- **Flammability**
  1. Flash point: 14 C (58 F) (closed cup)
  2. Autoignition temperature: 450 C (842 F)
  3. Flammable limits in air, % by volume: Lower: 2; Upper: 8
  4. Extinguishant: Dry chemical, carbon dioxide, alcohol foam
- **Warning properties**
  1. Odor Threshold: According to the *Handbook of Organic Industrial Solvents*, the odor of n-propyl acetate is detectable at the permissible exposure limit.
  2. Eye Irritation Level: The *Handbook of Organic Industrial Solvents* states that n-propyl acetate "causes irritation of mucous membranes at the threshold limit."
  3. Evaluation of Warning Properties: Through its odor and irritant effects, n-propyl acetate can be detected at the TLV. 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 n-propyl 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 n-propyl acetate may be used. An analytical method for n-propyl 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 n-propyl acetate.
- Clothing wet with liquid n-propyl acetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of n-propyl acetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the n-propyl acetate, the person performing the operation should be informed of n-propyl acetate's hazardous properties.
- Any clothing which becomes wet with liquid n-propyl acetate should be removed immediately and not reworn until the n-propyl acetate is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid n-propyl acetate may contact the eyes.

SANITATION

- Skin that becomes wet with liquid n-propyl acetate should be promptly washed or showered with soap or

mild detergent and water to remove any n-propyl acetate.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in spray, brush, or dip application of lacquers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during application of adhesives; manufacture of lacquers and adhesives	Local exhaust ventilation; general dilution ventilation
Use as a solvent for rubber; during application of solvent for plastics, nitrocellulose, and cellulosic derivatives and resins; during brush or dip applications of lacquers; during preparation of flavoring agents and perfumes	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 n-propyl 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 n-propyl acetate gets on the skin, promptly flush the contaminated skin with water. If n-propyl 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 n-propyl 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 n-propyl acetate has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the affected person to vomit by having him touch the back of the throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water). Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

• If n-propyl 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. n-Propyl acetate should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

n-Propyl 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 N-PROPYL ACETATE

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).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
8000 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 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 Propyl 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: $CH_3CH_2CH_2OH$
- Synonyms: n-Propyl alcohol; 1-propanol; ethyl carbinol
- Appearance and odor: Colorless liquid with a mild, non-residual, alcoholic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propyl alcohol is 200 parts of propyl alcohol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 500 milligrams of propyl alcohol per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propyl 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 propyl alcohol may cause mild irritation of the eyes, nose, and throat. Drowsiness, headaches, and incoordination may also occur. Swallowing propyl 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: Prolonged skin exposure may cause drying and cracking 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 propyl alcohol.

- **Recommended medical surveillance**

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

—Skin disease: Propyl 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 propyl 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 propyl 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 propyl 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**

The principal action of propyl alcohol is that of a mild narcotic, but it may also act as an upper respiratory tract irritant. Mice exposed to vapor developed ataxia in 90 to 120 minutes at 3250 ppm; deep narcosis occurred after 240 minutes' exposure at 4100 ppm. Propyl alcohol is absorbed, oxidized, and eliminated more rapidly than

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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is ethyl alcohol. Skin absorption has been demonstrated in animals, as well as mild irritation of the skin on repeated exposure due to defatting action. 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): 97 C (207 F)
  3. Specific gravity (water = 1): 0.8
  4. Vapor density (air = 1 at boiling point of propyl alcohol): 2.1
  5. Melting point: −126 C (−195 F)
  6. Vapor pressure at 20 C (68 F): 15 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): 1.3
- **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 propyl alcohol.
  4. Special precautions: Propyl alcohol will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 15 C (59 F) (closed cup)
  2. Autoignition temperature: 440 C (824 F)
  3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 13.5
  4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Both Summer and May report odor thresholds of 30 ppm.
  2. Eye Irritation Level: n-Propyl alcohol, according to Grant, resembles "ethyl alcohol in physical and toxic properties." Grant states that a vapor concentration of 2500 ppm has "no notable effect on the eyes." The AIHA *Hygienic Guide* notes that above 5500 ppm, some eye and nasal irritation occur.
  3. Evaluation of Warning Properties: Since the odor threshold of n-propyl alcohol is below the permissible exposure limit (200 ppm), 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 propyl 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 propyl alcohol may be used. An analytical method for propyl 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).

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

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation and use during spray application of surface coatings containing solvent, polystyrene coatings, and dopes	Local exhaust ventilation; personal protective equipment
Liberation during use as a chemical intermediate in organic synthesis	Local exhaust ventilation; general dilution ventilation
Use during printing on plastic film and sheeting with polyamide-based inks	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during textile and leather processing	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in application of surface coatings other than spray or heat in nitrocellulose lacquers, dopes, and polystyrene coatings	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture and packaging of surface coatings as a solvent in nitrocellulose lacquers, dopes, polystryrene coatings, inks, dyes, textiles, leather finishes, and artists' fixatives; manufacture of cleaning preparations and polishing agents	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in extraction of vegetable oils, castor oil, and pharmaceuticals; use during cleaning and degreasing operations	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during cellulose processing; spinning of acrylonitrile; manufacture of brake fluids	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 propyl 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 propyl alcohol gets on the skin, flush the contaminated skin with water. If propyl 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 propyl 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 propyl 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 propyl 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. Propyl alcohol should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Propyl 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

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RESPIRATORY PROTECTION FOR PROPYL ALCOHOL

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s).
2000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
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 Propylene Dichloride

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: $CH_3CHClCH_2Cl$
- Synonyms: 1,2-Dichloropropane
- Appearance and odor: Colorless liquid with an odor like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propylene dichloride is 75 parts of propylene dichloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 350 milligrams of propylene dichloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propylene dichloride 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 propylene dichloride causes eye and skin irritation and may cause drowsiness or lightheadedness.

2. Long-term Exposure: Prolonged overexposure to propylene dichloride may affect the liver and kidneys.

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 propylene dichloride.

- **Recommended medical surveillance**

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

—Skin disease: Propylene dichloride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Propylene dichloride is known as a liver toxin in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Propylene dichloride 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 propylene dichloride 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**

Propylene dichloride vapor is a narcotic and an eye irritant. At 2200 ppm for 7 hours, guinea pigs developed severe conjunctival swelling, as well as signs of respiratory irritation and incoordination; some died after 5 daily exposures, showing severe liver injury, some kidney injury, and occasional adrenal changes. Repeated inhalation of 1000 ppm caused some deaths among dogs after 24 exposures of 7 hours' duration, and among rats after only 7 exposures. There was early onset of lacrimation, eye irritation, and incoordination. Liver damage was the main finding in the animals that died. At 400 ppm, rats and guinea pigs exposed for up to 140

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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daily 7-hour exposures showed no ill effects and no histologic changes. However, of a group of C3H-strain mice exposed at 400 ppm, some died; others developed hepatomas, a finding of equivocal significance. Propylene dichloride is mildly irritating to human skin, and some skin absorption may occur from exposure to the liquid. The undiluted liquid is moderately irritating to the eyes but does not cause permanent injury.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 113
  2. Boiling point (760 mm Hg): 96.1 C (205 F)
  3. Specific gravity (water = 1): 1.16
  4. Vapor density (air = 1 at boiling point of propylene dichloride): 3.9
  5. Melting point: −100 C (−148 F)
  6. Vapor pressure at 20 C (68 F): 39.5 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.26
  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. Strong acids may cause decomposition.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide and hydrogen chloride) may be released in a fire involving propylene dichloride.
  4. Special precautions: Propylene dichloride will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 15.6 C (60 F) (closed cup)
  2. Autoignition temperature: 557 C (1035 F)
  3. Flammable limits in air, % by volume (at 100 C): Lower: 3.4; Upper: 14.5
  4. Extinguishant: Dry chemical, foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: May reports an odor threshold of 50 ppm. The AIHA *Hygienic Guide* states that "human subjects described the odor as 'strong' at 130 to 190 ppm and 'not noticeable' at 15 to 23 ppm."
  2. Eye Irritation Level: According to Grant, "exposure of guinea pigs to 2200 ppm in air for many hours until most were dead caused lacrimation and swelling of the lids and conjunctiva. To the extent that the corneas were left unprotected, bluish discoloration of the corneas and infection developed. Rabbits exposed to the same conditions showed little irritation." No quantitative information is available concerning the threshold of eye irritation. No ill effects have been observed in animals chronically exposed to 400 ppm.
  3. Evaluation of Warning Properties: Since the odor threshold of propylene dichloride is below the permissible exposure limit, this substance 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 propylene dichloride 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 propylene dichloride may be used. An analytical method for propylene dichloride 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).
PB 265 026).

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 propylene dichloride.
- Clothing wet with liquid propylene dichloride should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of propylene dichloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propylene dichloride, the person performing the operation should be informed of propylene dichloride's hazardous properties.

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

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

SANITATION

• Skin that becomes wet with liquid propylene dichloride should be promptly washed or showered with soap or mild detergent and water to remove any propylene dichloride.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as a soil fumigant for protection of fruit and nut crops, field crops, beets, and tobacco against nemotodes	Adequate ventilation; personal protective equipment
Use in cleaning, degreasing, and spot removal operations including paint and varnish removal	Local exhaust ventilation; personal protective equipment
Use during rubber compouding and vulcanizing operations	Local exhaust ventilation; personal protective equipment
Use during extraction processing of fats, oils, lactic acid, and petroleum waxes	Local exhaust ventilation; personal protective equipment
Use in the manufacture of tetrachloroethylene and propylene oxide	Local exhaust ventilation; personal protective equipment
Use as an additive and lead scavenger in antiknock fluids	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 propylene dichloride 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 propylene dichloride gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If propylene dichloride 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 propylene dichloride, 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 propylene dichloride 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 propylene 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, 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. Propylene dichloride should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Propylene dichloride 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 PROPYLENE DICHLORIDE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
400 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Propylene Imine*

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_7N
- Synonyms: 2-Methylaziridine
- Appearance and odor: Fuming, colorless liquid with a strong, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propylene imine is 2 parts of propylene imine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of propylene imine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Propylene imine 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: Overexposure to propylene imine causes eye irritation.

2. Long-term Exposure: Repeated doses fed to animals have been shown to cause 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 propylene imine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to propylene imine 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, breasts, eyes, nervous system, and blood should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Propylene imine has been shown to cause granulocytic leukemia in rats repeatedly exposed to oral doses as little as 10 mg/kg. 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**

Propylene imine vapor is a carcinogen in animals. This compound has also caused eye irritation. Exposure of rats to 500 ppm for 4 hours was fatal, but inhalation for 2 hours resulted in no deaths. Rats given 20 mg/kg by gavage twice weekly suffered from advanced flaccid paralysis after 18 weeks, and the mortality rate was high; at 10 mg/kg, paralysis occurred to a lesser extent after 30 weeks; granulocytic leukemia, squamous cell carcinoma of the ear duct, and brain tumors (glioma) were observed in different animals; females showed mammary adenocarcinomas, a number of which metastasized to the lung. When placed in the eye of a rabbit, a 5% aqueous solution produced corneal damage; it is also said to have caused injury to human eyes, but details have not been provided.

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: 57
  2. Boiling point (760 mm Hg): 66 C (151 F)
  3. Specific gravity (water = 1): 0.8
  4. Vapor density (air = 1 at boiling point of propylene imine): 2
  5. Melting point: −65 C (−85 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): Miscible in all proportions
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat; contact with acids
  2. Incompatibilities: Contact with acids will cause violent polymerization that may burst containers. 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 propylene imine.
  4. Special precautions: Liquid propylene imine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: −4 C (25 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 quantitative information is available.
  2. Eye Irritation Level: The ILO reports that "no industrial injuries (from propylene imine) have been reported, other than severe eye burns." According to Grant, the liquid "has caused severe damage when applied to rabbit eyes, similar in severity to 28% ammonium hydroxide." Patty reports that propylene imine causes acute effects which are similar to those caused by ethylene imine. Among the acute effects produced by ethylene imine are eye, nose, and throat irritation. For the purposes of this guideline, therefore, propylene imine is treated as an eye irritant.
  3. Evaluation of Warning Properties: Since there are no available quantitative data relating the warning properties of propylene imine 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**

At the time of publication of this guideline, no measurement method for propylene imine 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 propylene imine, where skin contact may occur.
- Clothing contaminated with propylene imine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of propylene imine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propylene imine, the person performing the operation should be informed of propylene imine's hazardous properties.
- Where exposure of an employee's body to liquid propylene imine 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 propylene imine or non-impervious clothing which becomes contaminated with propylene imine should be removed immediately and not reworn until the propylene imine 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 propylene imine contacting the eyes.
• Where there is any possibility that employees' eyes may be exposed to liquid propylene imine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with propylene imine should be immediately washed or showered to remove any propylene imine.
• Eating and smoking should not be permitted in areas where liquid propylene imine is handled, processed, or stored.
• Employees who handle liquid propylene imine 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 propylene imine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a polymer modifier to improve physical properties of polymer; to improve wet adhesion, brushability and freeze-to-thaw stability of paints, improve shrink-proofing agents of woolen textiles, and improve electrical properties of wire-coating materials	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of polypropylene imines and polymers for coating materials, adhesives, chelating agents, emulsifying agents, and fire-proofing agents in textile, rubber, paint, ink, and paper industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in pharmaceutical and chemical 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 propylene imine 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 propylene imine gets on the skin, immediately flush the contaminated skin with water. If propylene imine 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 propylene imine, 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 propylene imine 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 propylene imine is spilled or leaked, the following steps should be taken:
1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Dilute with water spray until no longer flammable. Add 4% acetic acid (vinegar) solution to the diluted spill until vinegar odor of acid is present, and flush the diluted and neutralized spill. Liquid propylene imine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.
• Waste disposal and neutralization methods:
Propylene imine may be disposed of:
1. By atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. If larger quantities, by diluting with water, then adding acetic acid in excess of that required to neutralize the propylene imine.

ADDITIONAL INFORMATION

To find additional information on propylene imine, look up propylene imine 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 PROPYLENE IMINE

Condition	Minimum Respiratory Protection* Required Above 2 ppm
Vapor 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.
500 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 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 propylene imine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Propylene 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: CH_3CHOCH_2
- Synonyms: 1,2-Epoxypropane; propene oxide; methyloxirane
- Appearance and odor: Colorless liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propylene oxide is 100 parts of propylene oxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 240 milligrams of propylene oxide 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 propylene oxide from 100 ppm to 20 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Effects of overexposure**

Overexposure to propylene oxide may cause irritation of the eyes, nose, throat, and lungs. Contact with propylene oxide liquid may cause skin or eye irritation or burns.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to propylene oxide.

- **Recommended medical surveillance**

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

—Skin disease: Propylene oxide can cause dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although propylene oxide 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 propylene oxide 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 propylene oxide 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**

Propylene oxide is a severe irritant and a mild depressant of the central nervous system. Excessive exposure of animals to vapors caused irritation of the eyes, upper respiratory tract, and lungs, as well as central nervous system effects characterized by ataxia, incoordination, and general depression. The LC50 for single exposures of rats was 3600 ppm, while 400 to 500 ppm was lethal

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 some rats on repeated daily exposures. The predominant effect was lung irritation and infection. All animals tolerated repeated exposures of 100 ppm without effects. Reported adverse effects on man have been confined to injury to the eyes, and skin. The vapor is irritating to the eyes and the liquid causes corneal burns. When confined to the skin, as from wearing contaminated clothing or shoes, the material and water solutions as dilute as 10% are likely to cause irritation, blistering, and even burns upon single, short exposures. Some evidence indicates that solutions more dilute than 10% may be more irritating than the undiluted propylene oxide. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 58
  2. Boiling point (760 mm Hg): 34 C (94 F)
  3. Specific gravity (water = 1): 0.83
  4. Vapor density (air = 1 at boiling point of propylene oxide): 2.0
  5. Melting point: −112 C (−170 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): 40.5
  8. Evaporation rate (butyl acetate = 1): 33.7
- **Reactivity**
  1. Conditions contributing to instability: Heat; contact with acids and caustics
  2. Incompatibilities: Anhydrous metal chlorides such as iron or aluminum chloride, strong acids, caustics, and peroxides cause polymerization with liberation of heat.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving propylene oxide.
  4. Special precautions: Propylene oxide will attack some forms of plastics, rubber, and coatings. No acetylide-forming metals such as copper or copper alloys should be in contact with propylene oxide.
- **Flammability**
  1. Flash point: −37 C (−35 F) (closed cup)
  2. Autoignition temperature: 748 C (1378 F)
  3. Flammable limits in air, % by volume: Lower: 2.1; Upper: 37.0
  4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Patty states that "the median detectable concentration of propylene oxide vapors is reported to be 200 ppm with 95% confidence limits of 114 to 353 ppm. The odor is described as sweet, alcoholic, and like natural gas, ether, or benzene."
  2. Eye Irritation Level: Grant reports that "exposure of monkeys and rabbits to 457 ppm of vapor in air for 7 hours daily had no adverse effect, but in rats and guinea pigs it irritated the eyes and induced lung edema."

The AIHA *Hygienic Guide*, Patty, the *Documentation of TLV's*, and several other sources all note that propylene oxide causes eye irritation. However, no quantitative information is available, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Patty states that "neither odor nor irritation can be relied upon to warn of the presence of vapor concentrations not suitable for prolonged and repeated exposure. Odor and/or irritation will warn of the presence of acutely dangerous concentrations." Since it appears that Patty considers any vapor concentrations above 100 ppm (the ACGIH threshold limit for 1961) "not suitable for prolonged and repeated exposure," propylene oxide is considered to have adequate warning properties for the purposes of this guideline. The median of the detectable odor concentrations (200 ppm) is only twice the permissible exposure limit. The chronic exposure data given in the *Documentation of TLV's* quoted below do not indicate that 200 ppm causes any toxic effects.

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 propylene oxide 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 propylene oxide may be used. An analytical method for propylene oxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of

respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid propylene oxide.

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

• Where there is any possibility of exposure of an employee's body to liquid propylene oxide, 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 propylene oxide or any clothing which becomes wet with liquid propylene oxide should be removed immediately and such clothing should not be reworn until the propylene oxide is removed from the clothing.

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

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in manufacture of polypropylene glycol and polyether polyols in production of polyurethane foam; manufacture of propylene glycol for use as a solvent, emulsifier, and mold inhibitor; manufacture of dipropylene glycol for use as a solvent, ink formulations, and glycol esters for solvents, oil additives, and hydraulic brake fluids	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in the production of lubricants, surfactants, and miscellaneous chemicals for pharmaceutical, petroleum, textile, rubber, and soap industries	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a low-boiling solvent for cellulose derivatives, hydrocarbons, commercial gums, and various resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a fumigant (moth-proofing agent), herbicide, germicide, insecticide, and stabilizer of vinyl resin lacquers and discoloration preventer of hydrocarbons	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a food preservative as a fungicide and fumigant	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during hydroxypropylating of wheat flour in order to modify it to mix readily with water	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 propylene oxide gets into the eyes, wash eyes 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**

If propylene oxide gets on the skin, immediately wash the contaminated skin with water if propylene oxide has not already evaporated. If propylene oxide 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 propylene oxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If propylene oxide 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 propylene 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, 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 may be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Propylene oxide should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Propylene oxide may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

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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 PROPYLENE OXIDE

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). A gas mask with a chin-style or a front- or back-mounted organic vapor canister.
2000 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 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 propylene 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 2000 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for n-Propyl Nitrate

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: $C_3H_8NO_3$
- Synonyms: None
- Appearance and odor: Colorless to pale yellow liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for n-propyl nitrate is 25 parts of n-propyl nitrate per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 110 milligrams of n-propyl nitrate per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

n-Propyl nitrate 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: Animal studies show that n-propyl nitrate causes temporary low blood pressure and may affect the ability of the blood to carry oxygen by forming methemoglobin. In man, methemoglobin formation may cause bluish discoloration of the skin, headache, weakness, drowsiness, nausea, rapid heart beat, shortness of breath, and unconsciousness.

2. Long-term Exposure: In animals repeated or prolonged exposure to n-propyl nitrate has caused irritation and thickness of the skin. It may also cause anemia.

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-propyl nitrate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to n-propyl nitrate 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, skin, nervous system, and kidneys should be stressed.

—A complete blood count: n-Propyl nitrate 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**

n-Propyl nitrate vapor causes anoxia due to the formation of methemoglobin. Exposure of rats to 10,000 ppm for 4 hours caused nasal irritation, dyspnea, methemoglobinemia, weakness, cyanosis, and death. In dogs repeatedly exposed to 260 ppm for 26 weeks, hemoglobinuria and mild anemia appeared during the first 2 weeks of exposure but then subsided. n-Propyl nitrate may induce hypotension in animals by direct action on vascular muscles. The liquid when placed into the eyes of rabbits caused mild transient inflammation with no evidence of corneal damage. The liquid applied to the skin of rabbits daily for 10 days caused staining, inflam-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

mation, and thickening of the skin but no evidence of systemic toxicity. n-Propyl nitrate has the potential to form methemoglobin in man; the effects of methemoglobinemia result from anoxia and include cyanosis especially evident in the lips, nose, and ear lobes; other effects are weakness, dizziness, and severe headache.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 105.1
  2. Boiling point (760 mm Hg): 111 C (231 F)
  3. Specific gravity (water = 1): 1.06
  4. Vapor density (air = 1 at boiling point of n-propyl nitrate): 3.6
  5. Melting point: Less than −101 C (−150 F)
  6. Vapor pressure at 20 C (68 F): 18 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 either strong oxidizers or with combustibles 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 n-propyl nitrate.
  4. Special precautions: n-Propyl nitrate will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 20 C (68 F) (closed cup)
  2. Autoignition temperature: 175 C (347 F)
  3. Flammable limits in air, % by volume: Lower: 2; Upper: 100
  4. Extinguishant: Foam, dry chemical
- **Warning properties**
  1. Odor Threshold: According to the *Documentation of TLV's*, "the odor is stated to be detectable at 50 ppm and above."
  2. Eye Irritation Level: n-Propyl nitrate is not known to be an eye irritant.
  3. Evaluation of Warning Properties: Since its odor threshold is only twice the permissible exposure limit, n-propyl nitrate 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 n-propyl nitrate may be used. An analytical method for n-propyl nitrate 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 n-propyl nitrate.
- Clothing wet with n-propyl nitrate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of n-propyl nitrate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the n-propyl nitrate, the person performing the operation should be informed of n-propyl nitrate's hazardous properties.
- Non-impervious clothing which becomes contaminated with n-propyl nitrate should be removed promptly and any clothing which becomes wet with liquid n-propyl nitrate should be removed immediately and not reworn until the n-propyl nitrate is removed from the clothing.

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

SANITATION

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

Operation	Controls
Use in liquid rocket propellants	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 n-propyl nitrate 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 n-propyl nitrate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid n-propyl nitrate 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 promptly.
• **Breathing**
If a person breathes in large amounts of n-propyl nitrate, 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 n-propyl nitrate 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 n-propyl nitrate 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, stir with a solution of sodium hydroxide or soda ash in water until oily layer disappears, then flush. Large quantities can be burned under the supervision of personnel qualified to dispose of explosives. Liquid n-propyl nitrate 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 n-propyl nitrate vapors are permitted.
• Waste disposal method:
n-Propyl nitrate may be disposed of as described above.

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RESPIRATORY PROTECTION FOR N-PROPYL NITRATE

Condition	Minimum Respiratory Protection* Required Above 25 ppm
Vapor Concentration	
250 ppm or less	Any chemical cartridge respirator with a cartridge containing non-combustible sorbents and providing protection against n-propyl nitrate. Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	Any chemical cartridge respirator with a full facepiece and a cartridge containing non-combustible sorbents and providing protection against n-propyl nitrate. A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against n-propyl nitrate. 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 containing non-combustible sorbents and providing protection against n-propyl nitrate. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Pyrethrum

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: The synonyms and molecular weights listed below correspond to the various components of pyrethrum whose formulas are listed here: 1) $C_{21}H_{28}O_3$; 2) $C_{22}H_{28}O_5$; 3) $C_{20}H_{28}O_3$; 4) $C_{21}H_{28}O_5$; 5) $C_{21}H_{30}O_3$; 6) $C_{22}H_{30}O_5$
- Synonyms: 1) Pyrethrin I; 2) Pyrethrin II; 3) Cinerin I; 4) Cinerin II; 5) Jasmolin I; 6) Jasmolin II
- Appearance and odor: Viscous brown resin or solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pyrethrum 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**

The chief effect from exposure to pyrethrum is skin rash particularly on moist areas of the skin. The rash may be associated with intense itching and blister formation. Hay fever-like symptoms, wheezing, and breathing difficulties may occur from exposure to this chemical. An allergic reaction causing weakness and collapse may occur in sensitive individuals. Pyrethrum may irritate the eyes. In animals, effects of intoxication include convulsions and paralysis.

- **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 pyrethrum.

- **Recommended medical surveillance**

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

—Chronic respiratory disease: In persons with chronic respiratory disease and especially asthma, the inhalation of pyrethrum might cause exacerbation of symptoms due to its sensitizing properties.

—Skin disease: Pyrethrum can cause dermatitis which may be allergic in nature. 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**

Pyrethrum dust causes dermatitis and occasionally sensitization. In animals, effects of intoxication are excitation, convulsions, muscular fasciculations, and tetanic paralysis. The chief effect in humans from exposure to pyrethrum is dermatitis. The usual lesion is a mild erythematous dermatitis with vesicles, papules in moist areas, and intense pruritis; a bullous dermatitis may develop. In a study of workers engaged in processing pyrethrum powder, 30% had erythema, skin roughening, and pruritis which subsided upon cessation of exposure. One of these workers had an anaphylactic type reaction; shortly after entering a dust laden room, the facial skin turned red and the person felt a sensation of burning and itching; the cheeks and eyes rapidly became swollen and pruritis became severe; the entire condition disappeared in 2 days after removal 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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National Institute for Occupational Safety and Health

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

exposure. Some persons exhibit sensitivity similar to pollinosis with sneezing, nasal discharge, and nasal stuffiness. A few cases of asthma due to pyrethrum mixtures have been reported; some of the individuals involved had a previous history of asthma with allergy to a wide spectrum of substances.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 1) 328.4; 2) 372.4; 3) 316.4; 4) 360.4; 5) 330.4; 6) 374.4;
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): 1 (approximately)
4. Vapor density (air = 1 at boiling point of pyrethrum): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None.
4. Special precautions: None.

- **Flammability**

1. Flash point: 82– 88 C (180– 190 F) (open cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Carbon dioxide, foam, dry chemical

- **Warning properties**

Since the vapor pressure of pyrethrum is essentially zero, warning properties are not considered.

Grant states that pyrethrum "is an insecticide powder which may cause allergic reaction and contact dermatitis. Transient conjunctival edema and hyperemia may be induced. The constituents pyrethrin I and II in pure form are said to be irritating to the eyes and mucous membranes. No persistent ocular disturbance from pyrethrum or its derivatives appears to have been reported."

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 pyrethrum 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).

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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 skin contact with pyrethrum or liquids containing pyrethrum where skin contact may occur.
- If employees' clothing may have become contaminated with pyrethrum or liquids containing pyrethrum, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with pyrethrum should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of pyrethrum from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pyrethrum, the person performing the operation should be informed of pyrethrum's hazardous properties.
- Non-impervious clothing which becomes contaminated with pyrethrum should be removed promptly and not reworn until the pyrethrum is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where pyrethrum or liquids containing pyrethrum may contact the eyes.

SANITATION

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

Operation	Controls
Application as an insecticide on pre- and post-harvest agricultural crops; cattle and poultry, food cartons, and confined areas	Good personal hygiene
Manufacture of pyrethrum	Good personal hygiene
Formulation of scabicides and parasiticides for medical and veterinary use	Good personal hygiene

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 pyrethrum or liquids containing pyrethrum 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 pyrethrum or liquids containing pyrethrum get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If pyrethrum or liquids containing pyrethrum 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 pyrethrum, 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 pyrethrum or liquids containing pyrethrum 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 pyrethrum 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:
Pyrethrum may be disposed of:
1. By making packages of pyrethrum in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving pyrethrum in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PYRETHRUM

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 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.
250 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. 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 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 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, 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 pyrethrum; 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 5000 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Pyridine

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_5N
- Synonyms: None
- Appearance and odor: Colorless or yellow liquid with a penetrating, sickening odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for pyridine is 5 parts of pyridine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 15 milligrams of pyridine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Pyridine 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 pyridine may cause irritation of the eyes, skin, and lining of the respiratory tract. Heavy exposure may also cause gastrointestinal disturbances with diarrhea, abdominal pain, and nausea, weakness, headache, dizziness, difficulty in sleeping, nervousness, and back pain with urinary frequency. Damage to the liver and kidneys may occur. There is some evidence that permanent central nervous system damage 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 pyridine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to pyridine 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. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Kidney damage has been reported from oral administration of pyridine to humans for therapeutic purposes. A urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Pyridine 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**

Pyridine vapor is a mild irritant to eyes and mucous membranes, and at high concentrations causes narcosis. In animals the major effects from administration of large doses by any route are local irritation and narcosis, while repeated feeding results in kidney and liver injury. Fatal injury to the liver and kidney has been reported from the prolonged oral administration of 1.8 to 2.5 ml daily for human therapeutic purposes. Workers exposed repeatedly to vapor concentrations averaging 125 ppm developed nausea and anorexia, as well as headache, dizziness, nervousness, and insomnia; in some cases, lower abdominal or back discomfort with urinary frequency was observed without associated evidence of liver or kidney damage. The possibility of permanent central nervous system injury is suggested by some case

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

reports. Chemical plant workers exposed to pyridine at a concentration of 6 to 12 ppm developed headache, temporary vertigo, nervousness, sleeplessness, nausea, and vomiting. In the eye of a rabbit a 40% solution caused corneal necrosis. Skin irritation may result from prolonged or repeated contact with the vapor and liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 79
  2. Boiling point (760 mm Hg): 115.3 C (239 F)
  3. Specific gravity (water = 1): 0.98
  4. Vapor density (air = 1 at boiling point of pyridine): 2.72
  5. Melting point: −42 C (−43.6 F)
  6. Vapor pressure at 20 C (68 F): 18 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 acids will 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 pyridine.
  4. Special precautions: Liquid pyridine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 20 C (68 F) (closed cup)
  2. Autoignition temperature: 482 C (900 F)
  3. Flammable limits in air, % by volume: Lower: 1.8; Upper: 12.4
  4. Extinguishant: Alcohol foam, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: Stern reports an odor threshold of 0.23 ppm, Summer reports 0.012 ppm, and May reports 0.013 ppm. The AIHA *Hygienic Guide*, however, notes that the odor "is an unreliable guide to concentrations exceeding 5 ppm. Olfactory fatigue occurs quickly."
  2. Eye Irritation Level: Grant reports that the vapor of pyridine is irritating to the eyes, but he gives no quantitative information.
  3. Other Information: Grant reports that pyridine vapors cause respiratory tract irritation, but no quantitative information is given. Persons who handle pyridine report that although olfactory fatigue occurs rapidly, a definite taste remains, thus giving adequate warning of exposure.
  4. Evaluation of Warning Properties: Although olfactory fatigue occurs rapidly upon exposure to pyridine, a definite taste remains. For this reason, pyridine 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 pyridine vapors using an adsorption tube with subsequent desorption with 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 pyridine may be used. An analytical method for pyridine 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 pyridine or solutions containing pyridine, where skin contact may occur.
- Clothing contaminated with pyridine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

pyridine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the pyridine, the person performing the operation should be informed of pyridine's hazardous properties.

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

SANITATION

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

Operation	Controls
Use in manufacture of pharmaceuticals such as antihistamines, vitamins, medicinals, CNS stimulants, and local anesthetics	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent in manufacture of polycarbonate resins used in hand tools, small appliances, camera parts, safety helmets, and electrical connectors	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a starting material in manufacture of chemical intermediates and products; use in manufacture of rubber accelerators, epoxy resins, and pharmaceuticals	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a solvent reaction medium or catalyst in paint manufacture, carbohydrate treatment, drug manufacture, and rubber manufacture; use as a reagent in chemical analysis	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in textile treatment as a water-proofing agent; use as a denaturant for ethyl alcohol; use as a coupling assistant in azo dye manufacture; use in purification of mercury fulminate in explosives manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
During thermal decomposition of flexible polyurethane foams	Personal protective equipment
Use as an inhibitor and for preparation of inhibitors; use in oil and gas well drilling	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 pyridine or solutions containing pyridine 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 liquid pyridine or solutions containing pyridine get on the skin, immediately flush the contaminated skin with water. If liquid pyridine or solutions containing pyridine penetrate through the clothing, remove the cloth-

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

• **Breathing**

If a person breathes in large amounts of pyridine, 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 pyridine 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 pyridine 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. Pyridine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Pyridine 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 PYRIDINE

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 full facepiece.
3600 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 3600 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 pyridine; 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 3600 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Quinone

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: OC_6H_4O
- Synonyms: p-Benzoquinone
- Appearance and odor: Pale yellow solid with an acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for quinone is 0.1 part of quinone per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of quinone per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Quinone 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**

If quinone comes in contact with the skin or the lining of the nose and throat, it may cause irritation, discoloration, redness, swelling, and blistering. Prolonged contact with the skin may cause ulceration. Contact with the eyes may cause irritation, discoloration, and damage which may produce vision difficulties and may be permanent.

- **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 quinone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to quinone 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 congenital or acquired eye defects would be expected to be at increased risk from exposure. Persons with poor visual acuity from high degrees of astigmatism, keratoconus, or pre-existing corneal injury should be excluded from repeated, uncontrolled exposure to quinone vapor. Examination of the eyes and skin should be stressed.

—Opthalmic examination: Quinone causes eye damage in humans. An opthalmic examination should be performed, including visual acuity and slit-lamp inspection of the cornea.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Quinone is a solid with appreciable vapor pressure, and the vapor or dust is very hazardous to the eyes. Acute exposure causes conjunctival irritation, and in some cases corneal edema, ulceration and scarring; transient eye irritation may be noted above 0.1 ppm and becomes marked at 1 to 2 ppm. Chronic exposure causes the gradual development of changes characterized as: (1) brownish discoloration of the conjunctiva and cornea confined to the intrapalpebral fissure, (2) small opacities of the cornea, and (3) structural corneal changes which result in loss of visual acuity. The pigmentary changes are reversible, but the more slowly developing structural changes in the cornea may progress. Although pigmentation may occur with less than 5 years of exposure, serious injury. Skin contact may cause irritation 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.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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

September 1978

this is uncommon and usually is not associated with serious injury. Skin contact may cause irritation and staining. Systemic effects from industrial exposure have not been reported. Skin cancer has been reported in mice painted with a quinone solution. A 0.1% or 0.25% solution of quinone in benzene was applied to the skin of mice daily or every other day; of 87 mice surviving for 200 days, 9 had papillomas of the skin, 3 had cancer of the skin, and 8 had lung cancer.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 108.1
  2. Boiling point (760 mm Hg): Sublimes
  3. Specific gravity (water = 1): 1.32
  4. Vapor density (air = 1 at boiling point of quinone): 3.7
  5. Melting point: 113 C (235 F)
  6. Vapor pressure at 20 C (68 F): 0.1 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 1.5
  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 quinone fumes and carbon monoxide) may be released in a fire involving quinone.
  4. Special precautions: Quinone will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: Data not available
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Water spray, dry chemical, carbon dioxide
- **Warning properties**
  1. Odor Threshold: According to the AIHA *Hygienic Guide*, the "odor of quinone is not readily apparent at 0.1 ppm." Grant, however, reports that the "vapors are perceptible by smell to human beings at about 0.1 ppm in air." According to the *Hygienic Guide*, olfactory fatigue occurs upon exposure to quinone.
  2. Eye Irritation Level: The *Hygienic Guide* states that "transient eye irritation may be noted above 0.1 ppm and becomes marked at 1 to 2 ppm." Grant states that "at 0.5 ppm the vapors are irritating to the eyes and at 3.0 ppm they are very irritating."
  3. Evaluation of Warning Properties: The *Hygienic Guide* states that "exposure evaluation by odor and irritant effects is not adequate to assure safety because: 1) the odor of quinone is not readily apparent at 0.1 ppm, 2) olfactory fatigue occurs, and 3) repeated exposure to levels causing sensory irritation may cause chronic eye injury." For these reasons, quinone is treated as a material with poor warning properties. The concentration of quinone 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 quinone 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 quinone, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with quinone, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where exposure of an employee's body to solid quinone or liquids containing quinone 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 quinone should be removed immediately and not reworn until the quinone 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 quinone or liquids containing quinone contacting the eyes.

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

SANITATION

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

• Workers subject to skin contact with quinone should wash with soap or mild detergent and water any areas of the body which may have contacted quinone at the end of each work day.

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

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

Operation	Controls
Use as an oxidizing agent in synthesis of organic chemicals and intermediates; in photography—developer hydroquinone; in agriculture in production of insecticides and fungicides; in pharmaceutical industry for production of cortisone and addition compound with barbituates	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer and resins industry as an inhibitor and retarder-antioxidant, curing agent, and catalyst	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a toner and intensifier in photographic industry; as a tanning agent for leather industry	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of quinhydrone electrodes for use for pH determinations	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 quinone or liquids containing quinone 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 quinone gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If quinone penetrates 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 quinone, 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 quinone 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 quinone 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:

Quinone may be disposed of:

1. By making packages of quinone in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving quinone 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 QUINONE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Particulate or Vapor Concentration	
5 ppm or 20 mg/m³ 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 300 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 75 ppm or 300 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 Rhodium Metal Fume and Dusts (as Rhodium)

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: Rh
- Synonyms: None
- Appearance: Gray fume or dust.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for rhodium metal fume and dusts is 0.1 milligram of rhodium metal fume and dusts (as rhodium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

None: See "Summary of toxicology."

- **Effects of overexposure**

1. *Short-term Exposure:* None known.
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 rhodium metal fume and dusts.

- **Recommended medical surveillance**

Routine medical examinations should be provided to each employee who is exposed to rhodium metal fume and dusts at potentially hazardous levels.

- **Summary of toxicology**

No toxic effects of rhodium metal fume and dusts have been reported from animal experiments or from observations on human beings.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 102.9
  2. Boiling point (760 mm Hg): Above 2500 C (4532 F)
  3. Specific gravity (water = 1): 12.4
  4. Vapor density (air = 1 at boiling point of rhodium metal fume and dusts): Not applicable
  5. Melting point: 1966 C (3570 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Rhodium metal fume and dusts are not known to be 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 rhodium metal fume and dusts on a filter, followed by

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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

September 1978

treatment with nitric acid, solution in hydrochloric acid, treatment with potassium bisulfate, and atomic absorption spectrophotometric analysis. An analytical method for rhodium metal fume and dusts 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 rhodium metal fume and dusts may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture of platinum alloys for use in thermocouples, windings for resistance furnaces, laboratory crucibles and catalysts for chemical processing, and preparation of dental castings	General dilution ventilation; local exhaust ventilation
Liberation during production and casting of rhodium powder during refining and recovery	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in applying thin reflective coatings by sublimation to scientific instruments, radio and radar equipment, searchlight reflectors, cinema projections, and headlight reflectors	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.

• **Breathing**

If a person breathes in large amounts of rhodium metal fume and dusts, 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 rhodium metal dust has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention.

SPILL AND DISPOSAL PROCEDURES

• If potentially hazardous amounts of rhodium metal fume and dusts are spilled or inadvertently released, 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 secured sanitary landfill.

• Waste disposal method:

Rhodium metal dusts may be disposed of in a secured sanitary landfill.

REFERENCES

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

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RESPIRATORY PROTECTION FOR RHODIUM METAL FUME AND DUSTS (AS RHODIUM)

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator.
1 mg/m³ or less	Any fume respirator or high efficiency particulate respirator. Any dust and mist respirator, except single-use or quarter-mask respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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

Occupational Health Guideline for Soluble Rhodium Salts (as Rhodium)

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 rhodium salts. Physical and chemical properties of one specific compound are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION—Hydrated rhodium trichloride

- Formula: $RhCl_3$-xH_2O
- Synonyms: Soluble rhodium trichloride; rhodium chloride
- Appearance and odor: Red-brown, odorless solid or liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble rhodium salts is 0.001 milligram of soluble rhodium salts (as rhodium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble rhodium salts may affect the body if they are inhaled or if they come in contact with the eyes or skin. They may also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: None known in humans

2. Long-term Exposure: None known in humans

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble rhodium salts.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble rhodium salts at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble rhodium salts exposure.

—Eye disease: Rhodium chloride has caused eye damage in animals. Persons with pre-existing eye disorders may be more susceptible to the effects of this agent.

—Kidney disease: Although rhodium 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.

—Central nervous system disorders: Rhodium trichloride has caused central nervous system damage in animals. Individuals with pre-existing central nervous system disorders may be more susceptible.

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

- **Summary of toxicology**

Toxicologic data on the soluble salts of rhodium are meager; however, solutions of salts splashed in the eye may cause mild irritation. Rhodium trichloride was found to have chemotherapeutic action against certain viruses in mice, but no mention was made of toxicity. The LD50 for rhodium trichloride in rabbits by intravenous injection was 215 mg/kg; the clinical signs presented shortly after injection were increasing lethargy and waning respiration. There were no abnormal findings at autopsy, and the rapid onset of death suggested central nervous system effects. A solution of rhodium chloride in a rabbit eye gave a delayed injurious reaction; a 0.1-M solution adjusted to pH 7.2 with ammonium hydroxide was placed for 10 minutes in a rabbit eye after the corneal epithelium had been removed; an orange color-

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

ation of the cornea occurred, which faded to faint yellow within 8 weeks. During the first 2 to 3 weeks, the cornea was slightly hazy; in the third week white opacities gradually developed, and finally there was extensive opacification and vascularization. Systemic effects have not been reported from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Hydrated rhodium trichloride**

1. Molecular weight: Greater than 209
2. Boiling point (760 mm Hg): 800 C (1472 F) (sublimes)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of soluble rhodium salts): Not applicable
5. Melting point: 100 C (212 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Less than 0.1 mm Hg
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: At temperatures above 100 C(212 F), some decomposition may occur.
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride or chlorine) may be released when rhodium trichloride decomposes.
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

The only rhodium salt for which information is available concerning toxic effects on the eye is rhodium chloride. Grant states that "rhodium chloride has been tested on a rabbit's eye and was found to give a peculiar delayed injurious reaction. A O.1-M clear, dark-red solution prepared and adjusted to pH 7.2 with ammonium hydroxide was applied for 10 minutes to the eye after the corneal epithelium had been removed by scraping. This exposure caused orange coloration of the cornea, fading to faint yellow in the course of 2 months. During the first 2 to 3 weeks the cornea was not opaque, but was slightly hazy. In the third week, however, irregular white opacities gradually developed. Ultimately the cornea became extensively opacified and vascularized."

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 rhodium salts on a filter, followed by treatment with nitric acid and perchloric acid, solution in aicd, and atomic absorption spectrophotometric analysis. An analytical method for soluble rhodium salts 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). Analytical Methods for Set M" (order number PB 265 029).

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 rhodium salts or liquids containing soluble rhodium salts.
- Clothing contaminated with soluble rhodium salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of soluble rhodium salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the soluble rhodium salts, the person performing the operation should be informed of soluble rhodium salts's hazardous properties.
- Non-impervious clothing which becomes contaminated with soluble rhodium salts should be removed promptly and not reworn until the soluble rhodium salts are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble rhodium salts or liquids containing soluble rhodium salts may contact the eyes.

SANITATION

• Skin that becomes contaminated with soluble rhodium salts should be promptly washed or showered to remove any soluble rhodium salts.
• Eating and smoking should not be permitted in areas where soluble rhodium salts or liquids containing soluble rhodium salts are handled, processed, or stored.
• Employees who handle soluble rhodium salts or liquids containing soluble rhodium salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during refining and extraction of metal from platinum ores	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in electroplating baths for finishing scientific instruments, camera fittings, radio equipment, and jewelry; use in laboratory for research	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 soluble rhodium salts or liquids containing soluble rhodium salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention.
• **Skin Exposure**
If soluble rhodium salts or liquids containing soluble rhodium salts get on the skin, flush the contaminated skin with water. If soluble rhodium salts or liquids containing soluble rhodium salts 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 rhodium salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
• **Swallowing**
When soluble rhodium salts or liquids containing soluble rhodium salts have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
• **Rescue**
Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
• If soluble rhodium salts are spilled, the following steps should be taken:
1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing soluble rhodium salts should be absorbed in vermiculite, dry sand, earth, or a similar material.
• Waste disposal method:
Soluble rhodium salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Rhodium as Rh," *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 RHODIUM SALTS (AS RHODIUM)

Condition	Minimum Respiratory Protection* Required Above 0.001 mg/m³
Particulate Concentration	
0.01 mg/m³ or less	Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
0.05 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.
1 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.
2 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 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.

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

Occupational Health Guideline for Ronnel

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: $(CH_3O)_2PSOC_6H_2Cl_3$
- Synonyms: Fenchlorphos; O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate
- Appearance and odor: White to tan waxy solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ronnel is 15 milligrams of ronnel per cubic meter of air (mg/m^3) averaged over an eight-hour work shift (*Federal Register*, Vol. 43, p. 57603, 8 December 1978).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Ronnel can affect the body if it is inhaled or if it comes in contact with the eyes. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Ronnel is one of the least toxic of the organophosphate insecticides. Very large exposures are required to cause symptoms. In animal experiments, ronnel has caused watering of the mouth, tremors, diarrhea, small pupils, and respiratory distress. Ronnel powder is irritating to the eye in rabbits.

2. Long-term Exposure: In animals ronnel has caused 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 ronnel.

- **Recommended medical surveillance**

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

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ronnel might cause exacerbation of symptoms due to an anticholinesterase effect.

—Liver disease: Ronnel 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: Ronnel 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**

Ronnel is a weak cholinesterase inhibitor. It affects primarily the pseudoesterases of the blood plasma rather than the erythrocyte acetylcholinesterase. In male rats, the oral LD50 was 1.7 g/kg; effects were salivation, tremors, diarrhea, miosis, and respiratory distress – all attributed to the anticholinesterase effect of ronnel. Rats fed 50 mg/kg body weight in the diet for 105 days developed slight liver and kidney damage. When a small amount of ronnel powder was placed in the eye of a rabbit, there were slight discomfort and transient conjunctival irritation which subsided within 48 hours. In an experiment on humans in which 50 subjects received 3 applications per week for 3 weeks 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.

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

gauze saturated with a 10% suspension of ronnel in sesame oil, there were no significant effects on the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 321.5
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 1.48
  4. Vapor density (air = 1 at boiling point of ronnel): Not applicable
  5. Melting point: 35 C (95 F)
  6. Vapor pressure at 20 C (68 F): 0.0008 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.0044
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: Temperatures above 150 C (300 F) may cause explosive decomposition and 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 sulfur dioxide, dimethyl sulfide, trichlorophenol, etc., and carbon monoxide) may be released when ronnel decomposes.
  4. Special precautions: Melted ronnel will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

Ronnel 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**

An analytical method for ronnel 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 ronnel or liquids containing ronnel.
- If employees' clothing may have become contaminated with ronnel or liquids containing ronnel, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with ronnel should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ronnel from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ronnel, the person performing the operation should be informed of ronnel's hazardous properties.
- Non-impervious clothing which becomes contaminated with ronnel should be removed promptly and not reworn until the ronnel is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where ronnel or liquids containing ronnel may contact the eyes.

SANITATION

- Skin that becomes contaminated with ronnel should be promptly washed or showered with soap or mild detergent and water to remove any ronnel.
- Eating and smoking should not be permitted in areas where solid ronnel is handled, processed, or stored.
- Employees who handle ronnel or liquids containing ronnel 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 ronnel may occur and control methods which may be effective in each case:

Operation	Controls
Use as an insecticide and pest control agent for agricultural and livestock operations	General dilution ventilation; personal protective equipment
Formulation of insecticides for agricultural and livestock use	General dilution ventilation; personal protective equipment
Use as an insecticide for fruits	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 ronnel or liquids containing ronnel 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 ronnel or liquids containing ronnel get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If ronnel or liquids containing ronnel 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 ronnel, 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 ronnel or liquids containing ronnel 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 ronnel 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. Molten ronnel should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Ronnel may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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

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RESPIRATORY PROTECTION FOR RONNEL

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, 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	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.
7500 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 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 gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Rotenone

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: $C_{23}H_{22}O_6$
- Synonyms: Rotenone, commercial; tubatoxin; "cube"; derrin
- Appearance and odor: Colorless to red, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Rotenone 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 rotenone may cause irritation of the eyes and skin. Symptoms of absorption of rotenone dust (inferred mostly from animal studies) include numbness of the mouth, nausea, vomiting, gastric pain, pulmonary irritation, trembling, loss of coordination, convulsions, stupor, and cessation of breathing. In animal experiments, exposure to rotenone dust has caused liver and kidney damage and has produced tumors.

- **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 rotenone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to rotenone 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, eyes, respiratory tract, and liver should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Rotenone dust affects the nervous system and causes convulsions in animals. Animals repeatedly fed derris powder (a botanical source containing 9.6% rotenone) at levels from 312 to 5000 ppm developed focal liver necrosis and mild kidney damage. Of 40 female rats given daily intraperitoneal injections of rotenone in sunflower oil of 1.7 mg/kg for 42 days, over 60% developed mammary tumors 6 to 11 months after the end of treatment; most of the tumors were mammary adenomas; one was a differentiated adenocarcinoma; none of the control animals had tumors when examined 19 months after treatment. The lethal oral dose in humans is estimated to be 0.3 to 0.5 g/kg. In humans, inhalation of dust is expected to cause pulmonary irritation. Symptoms of absorption in humans (inferred mostly from animal studies) may include numbness of oral mucous membranes, nausea, vomiting, and abdominal pain. There may be muscle tremors, incoordination, clonic convulsions, and stupor. The dust is irritating to the eyes and skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 394.4
  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): 1 (approximately)
4. Vapor density (air = 1 at boiling point of rotenone): Not applicable
5. Melting point: 163 C (325 F) or 181 C (358 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.00002
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: None.
4. Special precautions: None.

• **Flammability**

1. Flash point: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical, water.

• **Warning properties**

Since the vapor pressure of rotenone is negligible, warning properties are not considered.
Rotenone 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 rotenone 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 rotenone or liquids containing rotenone.

• If employees' clothing has had any possibility of being contaminated with rotenone or liquids containing rotenone, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with rotenone should be removed promptly and not reworn until the rotenone is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where rotenone or liquids containing rotenone may contact the eyes.

SANITATION

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

• Eating and smoking should not be permitted in areas where rotenone or liquids containing rotenone is handled, processed, or stored.

• Employees who handle rotenone or liquids containing rotenone 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 rotenone may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticides	Process enclosure; local exhaust ventilation; wet methods
Application on agricultural crops and livestock as an insecticide and ascaricide	Personal protective equipment
Manufacture of rotenone	Process enclosure; local exhaust ventilation; wet methods; 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 rotenone or liquids containing rotenone 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 rotenone or liquids containing rotenone get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If rotenone or liquids containing rotenone 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 rotenone, 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 rotenone or liquids containing rotenone 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 rotenone 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 can 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:

Rotenone may be disposed of

1. By making packages of rotenone in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving rotenone in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR ROTENONE (COMMERCIAL)

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 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.
250 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.
5000 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 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, 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 Selenium and Its Inorganic Compounds (as Selenium)*

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 selenium and its inorganic compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Selenium

- Formula: Se
- Synonyms: Selenium, metallic; selenium, elemental
- Appearance and odor: Black, gray, or red odorless solid.

Sodium selenite

- Formula: Na_2SeO_3
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Sodium selenate

- Formula: Na_2SeO_4
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium dioxide

- Formula: SeO_2
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium oxychloride

- Formula: $SeOCl_2$
- Synonyms: None
- Appearance: Colorless to yellow liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium and its inorganic compounds is 0.2 milligram of selenium and its inorganic compounds (as selenium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Selenium, sodium selenite, sodium selenate, or selenium dioxide can affect the body if they are inhaled, if they come in contact with the eyes or skin, or if they are swallowed. Selenium oxychloride and selenium dioxide may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Inhalation of large quantities of selenium dioxide or selenium oxychloride may cause severe breathing difficulties which may not appear for several hours after exposure. Skin contact with selenium dioxide or selenium oxychloride may cause skin burns. Skin exposure to selenium dioxide dust may cause a skin rash. Splashes of selenium dioxide may cause eye irritation. Selenium dioxide dust may cause "rose eye," an allergy of the eyelids in which they may become puffy.

2. Long-term Exposure: Prolonged exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide may cause paleness, coated tongue, stomach disorders, nervousness, metallic taste and a garlic odor of the breath. Fluid in the abdominal cavity, damage to the liver and spleen, and anemia have been reported in animals. Prolonged skin contact with selenium oxide or selenium oxychloride may cause skin sensitization.

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. 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 selenium and its inorganic compounds.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium and its inorganic 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 selenium, or with a history of other chronic respiratory disease, gastrointestinal disturbances, disorders of liver or kidneys, or recurrent dermatitis would be expected to be at increased risk from exposure. Examination of the eyes, respiratory system, liver, kidneys, and blood should be stressed. The skin should be examined for evidence of chronic disorders. Special consideration should be given to women of childbearing age since the possibility that selenium may be teratogenic might place these women in a high risk group.

—Urinalysis: Proper function of the kidneys is necessary to validate levels of selenium in the urine. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Selenium causes liver damage and tumors in animals. 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**

Elemental selenium and certain selenium compounds as dusts, vapors, and fumes irritate the eyes, upper respiratory tract, and skin. Animals exposed to selenium anhydride at a concentration of 150 mg/m^3 for 4 hours developed conjunctivitis, pulmonary edema, and convulsions preceding death; there were degenerative changes in the liver, kidneys, spleen, and heart. Prolonged feeding of animals with diets containing selenium in amounts of 5 to 15 ppm caused hepatic necrosis, hemorrhage, and cirrhosis; marked and progressive anemia occurred in some species. The possibility of teratogenic effects from exposure to selenium has been raised, based upon observations in animals, but it has not been established in man. Eleven of 53 rats developed adenoma or low-grade carcinoma in cirrhotic livers, and four others had advanced adenomatoid hyperplasia, after having survived for 18 to 24 months on diets containing 5, 7, or 10 ppm of selenium; no tumors occurred in 73 rats surviving less than 18 months, although after 3 months cirrhosis was frequent. In control rats 18 to 24 months of age, the incidence of spontaneous hepatic tumors was less than 1%. A group of workers briefly exposed to high concentrations of selenium fume developed severe irritation of the eyes, nose, and throat, followed by headaches; transient dyspnea occurred in one case. In workers exposed to an undetermined concentration of selenium oxide there was bronchospasm and dyspnea, followed within 12 hours by chills, fever, headache, and bronchitis, leading to pneumonitis in a few cases; all were asymptomatic within a week. In a study of workers in a selenium plant, workroom air levels ranged from 0.2 to 3.6 mg/m^3, while urinary levels ranged from below 0.10 to 0.43 mg/l; the chief complaints were garlic odor of the breath, metallic taste, gastrointestinal disturbances, and skin eruptions. An accidental spray of selenium dioxide, in unspecified form and concentration, into the eyes of a chemist caused superficial burns of the skin and immediate irritation of the eyes; within 16 hours vision was blurred, and the lower portions of both corneas appeared dulled; 16 days after the accident the corneas were normal. Acute burns of the skin can be caused by selenium oxychloride and selenium oxide, which are highly vesicant. Contact with the fume of heated selenium dioxide caused an acute, weeping dermatitis, with the development of hypersensitivity in some cases.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Selenium**

1. Molecular weight: 78.96
2. Boiling point (760 mm Hg): 685 C (1265 F)
3. Specific gravity (water = 1): 4.45 to 4.8
4. Vapor density (air = 1 at boiling point of selenium): Not applicable
5. Melting point: 150 C (302 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): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenite**

1. Molecular weight: 173
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1
4. Vapor density (air = 1 at boiling point of sodium selenite): Not applicable
5. Melting point: 710 C (1310 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mg Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 85
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenate**

1. Molecular weight: 188.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1

4. Vapor density (air = 1 at boiling point of sodium selenate): Not applicable

5. Melting point: Decomposes

6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg

7. Solubility in water, g/200 g water at 20 C (68 F): 83

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Selenium dioxide**

1. Molecular weight: 110.9

2. Boiling point (760 mm Hg): 315 C (599 F) (sublimes)

3. Specific gravity (water = 1): 3.95

4. Vapor density (air = 1 at boiling point of selenium dioxide): Not applicable

5. Melting point: 340 C (644 F)

6. Vapor pressure at 20 C (68 F): 0.001 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 257

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Selenium oxychloride**

1. Molecular weight: 165.9

2. Boiling point (760 mm Hg): 176 C (349 F)

3. Specific gravity (water = 1): 2.42

4. Vapor density (air = 1 at boiling point of selenium oxychloride): 5.7

5. Melting point: 10.8 C (51 F)

6. Vapor pressure at 20 C (68 F): 0.35 mm approximately

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

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None hazardous

2. Incompatibilities: Contact of selenium with acids may cause formation of poisonous hydrogen selenide gas. Contact of selenium with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving selenium, sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride.

4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable

2. Autoignition temperature: Selenium: Data not available; sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride: Not applicable

3. Flammable limits in air, % by volume: Not applicable

4. Extinguishant: For selenium, water

• **Warning properties**

The *Documentation of TLV's* notes that "Clinton reported intense irritation of eyes, nose, and throat, followed by headache, in a group of workers briefly exposed to high concentrations of selenium fume." The ILO reports that "persons who work in atmospheres containing selenium dioxide dust may develop a condition known among the workers as 'rose eye,' a pink allergy of the eyelids, which often become puffy. There is usually also a conjunctivitis of the palpebral conjunctiva but rarely of the bulbar conjunctiva." The *Hygienic Information Guide* for selenium states that "in contact with the eye, selenium compounds exert a rapid irritant action leading to inflammation." Grant reports that both selenium dioxide and selenium sulfide can produce toxic effects on the eye. Quantitative information concerning air concentrations of selenium compounds which cause eye irritation 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 selenium and its inorganic compounds on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for selenium and its inorganic 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 any possibility of skin contact with selenium oxychloride or liquids containing selenium oxychloride.
- 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 selenium, sodium selenite, sodium selenate, or liquids containing these compounds.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with selenium dioxide or liquids containing selenium dioxide, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with selenium oxychloride, sodium selenite,sodium selenate, selenium dioxide, 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 selenium oxychloride, sodium selenite, sodium selenate, or selenium dioxide 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 selenium, selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, 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 selenium, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with selenium oxychloride should be removed immediately and not reworn until the selenium oxychloride 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 selenium dioxide, selenium oxychloride, or liquids containing these compounds contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium selenite, sodium selenate, or liquids containing these compounds may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to selenium oxychloride, selenium dioxide, 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 selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash any areas of the body which may have contacted selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds at the end of each work day.
- Skin that becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these substances should be promptly washed or showered to remove any contaminant.
- Skin that becomes contaminated with selenium oxychloride should be immediately washed or showered to remove any selenium oxychloride.
- Eating and smoking should not be permitted in areas where selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds 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 selenium and its inorganic compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining recovery, and purification and manufacture of selenium compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in glassware industry for decolorization of fiberglass, scientific glassware, vehicular tail lights, traffic and other signal lenses, and infrared equipment; use in manufacture of electrical components in welding, transformers, semiconductors, photoelectric cells, etc.	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of photography and photocopy devices; manufacture of dyes, pigments, and colored glazes for metal etching and for printing on glass	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of lubricating oils and extreme pressure lubricants as antioxidants and detergency improvers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber industry for manufacture and use as vulcanization accelerators and antioxidants; use in manufacture of pharmaceuticals, fungicides, and dermatitis control	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst for hardening fats for soaps, waxes, edible fats, and plastics	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of insecticides, parasiticides, bactericides, and herbicides for agricultural and citrus crops	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of flame-proofing agents on textiles and electric cables	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of delayed action blasting caps	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as solvents in paint and varnish removers; rubber, resin, and glue solvent; use for organic synthesis in oxidation, hydrogenation, and dehyrogenation	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in refining of copper, silver, gold, or nickel ores or during recycling of scrap metal	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous operations in manufacture of insect repellants, activators, hardeners, special ceramic materials, plasticizers, and mercury vapor detectors	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use for preparation of feed additives for poultry and swine	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 selenium or its inorganic 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 selenium or its inorganic compounds get on the skin, immediately wash the contaminated skin. If selenium, sodium selenite, sodium selenate, or selenium dioxide soak through the clothing, remove the clothing immediately and wash the skin. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of selenium sodium selenite, sodium selenate, or selenium 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 selenium, sodium selenite, sodium selenate, selenium oxychloride, or selenium dioxide 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 selenium or its inorganic 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. Liquid containing selenium and its inorganic compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Selenium and its inorganic compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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* SPECIAL NOTE

Selenium and its inorganic compounds (as selenium) 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).

RESPIRATORY PROTECTION FOR SELENIUM AND ITS INORGANIC COMPOUNDS (AS SELENIUM)

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m³
Particulate Concentration	
10 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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. A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
Greater than 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	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus with a full facepiece.

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

Occupational Health Guideline for Selenium Hexafluoride

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: SeF_6
- Synonyms: None
- Appearance: Colorless gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium hexafluoride is 0.05 part of selenium hexafluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of selenium hexafluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Selenium hexafluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Animal experiments have shown selenium hexafluoride to be a severe respiratory irritant which has produced severe breathing difficulties. These breathing difficulties may be delayed in onset.

- **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 selenium hexafluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium hexafluoride 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 should be stressed.

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

—FVC and FEV (1 sec): Selenium hexafluoride is a severe pulmonary irritant in animals. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Pericdic 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**

Selenium hexafluoride gas is a severe respiratory irritant in animals. Exposure of four animal species to 10 ppm for 4 hours was fatal; 5 ppm for 4 hours was not fatal but caused pulmonary edema, while 1 ppm produced no effects. Animals exposed to 5 ppm for 1 hour daily for 5 days developed signs of pulmonary injury; 1 ppm for the same time period caused no detectable effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 193
2. Boiling point (760 mm Hg): −35 C (−31 F)
3. Specific gravity (water = 1): 2.3 (liquid)
4. Vapor density (air = 1 at boiling point of selenium hexafluoride): 6.7
5. Melting point: −39 C (−38 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; reacts slowly

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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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8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: Data not available
4. Special precautions: None

• **Flammability**

1. Not combustible
2. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of selenium hexafluoride.
2. Eye Irritation Level: There is no indication in the available toxicological information that selenium hexafluoride produces eye irritation. Concerning fluorides, however, Grant states that "irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m^3 of air."
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of selenium hexafluoride, this compound is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure selenium hexfluoride may be used. An analytical method for selenium hexafluoride 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 selenium hexafluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a gaseous electric insulator	Process enclosure; local exhaust ventilation; personal protective equipment
Use during production of selenium hydroxide and hydrofluoric acid, selenium and nitrogen	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 selenium hexafluoride, 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 selenium hexafluoride is leaked, the following steps should be taken:

1. Ventilate area of leak.
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.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Selenium Hexafluoride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Selenium and Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1959.
- 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.

RESPIRATORY PROTECTION FOR SELENIUM HEXAFLUORIDE

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.
2.5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 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 providing protection against selenium hexafluoride. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Amorphous Silica

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: SiO_2
- Synonyms: Diatomite; silicon dioxide (amorphous); diatomaceous earth; diatomaceous silica
- Appearance and odor: Colorless to gray odorless powder.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for amorphous silica is 20 million particles of amorphous silica per cubic foot of air (mppcf) averaged over an eight-hour work shift, or the quotient of 30 mg/m³ divided by the percent of silica present. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for amorphous silica from 20 mppcf to 6 mg/m³ total dust (all sampled dust) and 3 mg/m³ for respirable dust.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Amorphous silica can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

Prolonged inhalation of amorphous silica including uncalcined diatomaceous earth may produce x-ray changes in the lungs without disability. Prolonged inhalation of calcined diatomaceous earth may cause silicosis with scarring of the lungs, cough, and shortness of breath.

- **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 amorphous silica.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to amorphous silica 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: Although the contribution of amorphous silica including natural diatomaceous earth to the development of pneumoconiosis is unclear, surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Since persons with impaired pulmonary function may be at increased risk from exposure to amorphous silica, periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Amorphous silica, including natural diatomaceous earth, is usually considered to be of low toxicity; however, pure amorphous silica is rarely found, and diatomaceous earth usually contains some amount of crystalline silica. When converted partially to a crystalline form by calcination, the dust of diatomaceous earth produces pulmonary fibrosis. Repeated exposure of guinea pigs to natural diatomaceous earth for periods up to 50 weeks to average concentrations ranging from 60 to 124 mg/m³ caused thickening of the alveolar septa by infiltration of macrophages, accumulation of large numbers of multinuclear cells containing dust particles, and lymphadenopathy, but no proliferation of connective tissue. In a study of diatomaceous earth 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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those employed in the quarry for more than 5 years and exposed only to natural diatomaceous earth had no significant roentgenologic changes; of others employed for more than 5 years in the milling process and exposed to calcined material, 17% had simple pneumoconiosis and 23% had the confluent form, probably the result of fibrogenic action of the crystalline silica formed by calcination of the naturally occurring mineral. In humans, calcined diatomaceous earth pneumoconiosis is characterized roentgenographically by fine linear and/or minute nodular shadows, either or both of which may be accompanied by conglomerate fibrosis; in the simple phase of the disease, the upper lobes, are affected more than the lower lobes and the condition progresses by an increase in the apparent number of the nodules, which rarely attain the density or size of nodules often seen in quartz silicosis. In the early confluent stage of the disease, the linear and nodular changes in the upper lung fields become more circumscribed and homogeneous; histologically, there is an absence of the focal, discrete, hyaline nodules or the whorled pattern of collagenous fibers of typical silicosis. The majority of experimental rats exposed to synthetic submicron amorphous silica at 1.5 mg/ft³ of air died from pulmonary vascular obstruction coupled with pulmonary insufficiency. Rats that survived recovered almost completely after 6 months.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 60.1
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 2.65
  4. Vapor density (air = 1 at boiling point of amorphous silica): Not applicable
  5. Melting point: 1700 C (3100 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with fluorine, oxygen dilfuoride, and chlorine trifluoride will cause fire.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Grant states that "particles of silica predominantly in the range of 2u to 3u introduced into the corneal stroma of rabbit eyes cause very little reaction."

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 amorphous silica in an impinger, followed by dust counting utilizing an optical microscope. An analytical method for amorphous silica 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.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during preparation by crushing, screening, calcining, and packing operations for industrial processes	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during mining and quarrying operations in extraction	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Use in manufacture of insulating materials including firebrick, insulation blocks, pipe covering, roofing felt, and asbestos panels	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a filter medium in food and beverage manufacture including sugar refining, brewing, wine and spirit manufacture, soft drinks, and purification of oils and fats	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of construction bonding materials including stucco, concrete, cement, plaster, and asphalt; manufacture of abrasive cleaning and polishing agents including scouring and polishing soaps and powders	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of surface coatings as porous extender and flattening agent in paint; as a filler agent for paints, lacquers, and varnishes; filler in paper manufacture, agricultural chemicals, and mineral filler in manufacture of plastics and vinyls	Process enclosure; local exhaust ventilation; personal protective equipment
Use in dry grinding operations including grinding and polishing with natural abrasive wheels; manufacture of absorbent floor cleaning agents for use in industry, refineries, and gas stations; use as a parting powder in foundry operations	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of pharmaceuticals and as a constituent of pill masses, dentifrices, and salves; use in pottery manufacture in glazes and bodies; use in water treatment; use as a carrier for nickel catalysts in petroleum and petrochemical industries	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 amorphous silica including diatomaceous earth 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.

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 amorphous silica is spilled or potentially hazardous quantities are released, the following steps should be t

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 secured sanitary landfill.

• Waste disposal method:

Amorphous silica may be disposed of in a secured sanitary landfill.

REFERENCES

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

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RESPIRATORY PROTECTION FOR AMORPHOUS SILICA (INCLUDING NATURAL AND DIATOMACEOUS EARTH)

Condition	Minimum Respiratory Protection* Required Above 20 mppcf
Particulate Concentration	
100 mppcf or less	Any dust and mist respirator.
200 mppcf 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.
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 Crystalline Silica

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: SiO_2
- Synonyms: Quartz; coesite; cristobalite; tridymite
- Appearance and odor: Colorless, odorless solid. (Crystalline silica may be a component of many mineral dusts).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for crystalline silica is (for respirable dust) 10 milligrams silica per cubic meter of air (mg/m^3) divided by the percent SiO_2 2 averaged over an eight-hour work shift, and(for total dust) 30 mg/m^3 divided by the percent SiO_2 2 averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit changed to 50 micrograms respirable free silica per cubic meter of air (ug/m^3) averaged over a work shift of up to 10 hours per day, 40 hours per week. Uncontrolled abrasive blasting with silica sand presents such a severe silicosis hazard that NIOSH has recommended that silica sand, or other materials containing more than one percent free silica, be prohibited as an abrasive substance in abrasive blasting operations. The NIOSH Criteria Document for Crystalline Silica should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Crystalline silica can affect the body if it is inhaled.

- **Effects of overexposure**

Exposure to crystalline silica dust may cause scarring of the lungs with cough and shortness of breath. This is called "Silicosis."

- **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 crystalline silica.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to crystalline silica 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 cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Crystalline silica causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Crystalline silica 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**

Crystalline silica or quartz dust causes silicosis, a form of disabling, progressive, and sometimes fatal pulmonary fibrosis characterized by the presence of typical nodulation in the lungs. The earliest lesions are seen in the region of the respiratory bronchioles. Lymphatics become obliterated by infiltration with dust-laden macrophages and granulation tissue. Morphologically, the typical lesion of silicosis is a firm nodule composed of concentrically arranged bundles of collagen. These nodules usually measure between 1 to 10 mm in diameter and appear around blood vessels and beneath the pleura, as well as in mediastinal lymph nodes. There

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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may be conglomeration of nodules as the disease progresses, leading to massive fibrosis. Histologically, the silicotic nodule consists of a relatively acellular, avascular core of hyalinized reticulin fibers arranged concentrically and blending with collagen fibers toward the periphery, which has well-defined borders. The particles of silica responsible for the reaction are birefringent and can be visualized under polarized light if they exceed 1 micrometer in diameter. Silica in the lungs can be identified by x-ray diffraction studies and by incinerating a portion of the lung, with subsequent analysis of the ash. The silica content of the normal lung should not exceed 0.2% dry weight. The clinical signs and symptoms of silicosis tend to be progressive with continued exposure to quantities of dust containing free silica, with advancing age, and with continued smoking habits. Symptoms may also be exacerbated by pulmonary infections and cardiac decompensation. Symptoms include cough, dyspnea, wheezing, and repeated nonspecific chest illnesses. Impairment of pulmonary function may be progressive. In individual cases there may be little or no decrement when simple discrete nodular silicosis is present, but when nodulations become larger or when conglomeration occurs, recognizable cardiopulmonary impairment tends to occur. Progression of symptoms usually continues after dust exposure ceases. While there may be a factor of individual susceptibility to a given exposure to silica dust, the risk of onset and the rate of progression of the pulmonary lesion is clearly related to the character of the exposure (dust concentration and duration). The disease tends to occur after an exposure measured in years rather than months. Occasionally, exposures to very high concentrations occur in short periods of time in occupations such as sandblasters and tunnel workers; in these cases of acute or rapidly-developing silicosis there may be severe respiratory symptoms resulting in death. It is generally accepted that silicosis predisposes to active tuberculosis, and that the combined disease tends to be more rapidly progressive than uncomplicated silicosis. A group of 972 granite-shed workers was studied to relate exposure levels to incidence of silicosis. The workers were grouped according to average exposure levels: 3 - 9, 20, 27 - 44, 37-60 particles per cubic foot (mppcf). Those with the highest dust exposure showed development of early silicosis in 40% of the workers after 2 years and 100% after 4 years of exposure. The development of silicosis in the remaining workers appeared to be proportional to the dust exposure. At the second highest exposure level (27-44 mppcf), early stages of silicosis appeared after 4 years of exposure and more advanced stages developed by the seventh year. In the group exposed at an average of 20 mppcf there was little indication of severe effects upon the health of the workers. In the lowest exposure group, where the average dust concentration was 6 mppcf (range 3 to 9 mppcf), there was no indication of any untoward effects of dust exposure on workers.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 60.1
  2. Boiling point (760 mm Hg): 2230 C (4046 F)
  3. Specific gravity (water = 1): 2.2 – 3.0
  4. Vapor density (air = 1 at boiling point of crystalline silica): Not applicable
  5. Melting point: 1600 C (2912 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with powerful oxidizing agents such as fluorine, chlorine trifluoride, manganese trioxide, oxygen difluoride, etc. may cause fires.
  3. Hazardous decomposition products: None
  4. Special precautions: Crystalline silica is attacked by hydrogen fluoride (or hydrofluoric acid).
- **Flammability**
  1. Not combustible
- **Warning properties**

Grant states that crystalline silica "has been observed to cause fibrotic nodules in the eye analogous to pulmonary silicosis. Particles of silica predominantly in the range of 2u to 3u introduced into the corneal stroma of rabbit eyes cause very little reaction. The same particles introduced into the anterior chamber sink to the bottom of the chamber and in the course of three to five weeks cause an inflammatory reaction with formation of fibrotic nodules in the iridocorneal angle. The reaction is quite different and more severe than that induced by brickdust, glass, or magnesium silicate . . . .

"An apparently unique report of involvement of the cornea in foundry workers who developed pulmonary silicosis has described gradual decrease in visual acuity due to corneal opacities in the pupillary area and has reported spectroscopic analytical evidence of an abnormally high silicon content in 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**

Sampling and analyses may be performed by collection of crystalline silica on a filter, followed by an x-ray diffraction analysis. A detailed analytical method for

diffraction analysis. An analytical method for crystalline silica 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 crystalline silica may occur and control methods which may be effective in each case:

Operation	Controls
Use in metallurgy industry for foundry molds, iron and steel castings, flux in smelting basic ores	Local exhaust ventilation; general dilution ventilation; wet process; personal protective equipment
Use in manufacture of fiberglass for electrical insulation, chemical filtration, and reinforcing fabrics	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from refining of sand for production of quartz	Process enclosure; local exhaust ventilation; water spray; personal protective equipment
Use in ceramics industry; use as an abrasive in scouring and polishing soaps and powders, flint sand paper, metal polishes, and sand blast work	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in processing synthetic quartz	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of refractories and building products; use in manufacture of electrical instruments for piezoelectric properties	Local exhaust ventilation; general dilution ventilation; wet process; personal protective equipment
Use in grading and classification of electronic and optical grade quartz	Local exhaust ventilation; general dilution ventilation
Use in manufacture of optical equipment in prisms, wedges, and lenses	Local exhaust ventilation; general dilution ventilation; wet process; personal protective equipment
Use in a variety of processes as paint extender, lining for acid towers, in the chemical industry in dental composition, in rocket engines and spacecraft, and graining lithographic plates	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during granite and similar material processing	Local exhaust ventilation; general dilution ventilation; wet process; 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 crystalline silica dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of crystalline silica 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 spills or releases until cleanup has been completed.

• If crystalline silica 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 secured sanitary landfill.

• Waste disposal method:

Crystalline silica may be disposed of in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on crystalline silica, look up crystalline silica in the following documents:

• Medical Surveillance for Chemical Hazards

• Respiratory Protection for Chemical Hazards

• Personal Protection and Sanitation for Chemical Hazards

• NIOSH Criteria Document for Crystalline Silica (November 1974)

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 CRYSTALLINE SILICA

Condition	Minimum Respiratory Protection* Required Above X** mg/m³
Particulate Concentration	
5X** mg/m³ or less	Any dust respirator.
10X** 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.
50X** 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.
500X** 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 500X** 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.

**X indicates the permissible exposure as defined above.

Occupational Health Guideline for Silver Metal and Soluble Silver 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 metallic silver and all soluble silver compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Silver, metallic

- Formula: Ag
- Synonyms: None
- Appearance and odor: Characteristic white metallic solid with no odor.

Silver nitrate

- Formula: $AgNO_3$
- Synonyms: Argerol; lunar caustic
- Appearance and odor: Colorless and odorless solid which may become gray on storage.

Silver fluoride

- Formula: AgF
- Synonyms: None
- Appearance and odor: Yellow-white, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for silver metal and soluble silver compounds is 0.01 milligram of silver metal and soluble silver compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for silver metal and soluble silver compounds from 0.01 mg/m^3 to 0.1 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Silver or soluble silver 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**

Silver or soluble silver compounds can cause discoloration or blue-gray darkening of the eyes, nose, throat, and skin. Silver nitrate is strongly corrosive and can cause burns and permanent damage to the eyes and can burn the skin.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to silver metal or soluble silver compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to silver metal and soluble silver compounds at potentially hazardous levels:

1. Initial Medical Examination:

—Examination of the nasal septum, eyes, and skin for evidence of pigmentation: The purpose is to establish a baseline for future observations of silver deposition in tissues.

2. Periodic Medical Examination: The aforementioned

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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medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

The dust of silver and its soluble compounds cause argyria, the local or generalized impregnation of the mucous membranes, skin, and eyes with silver. Localized argyria occurs in the skin, eyes, nasal septum and throat, where gray-blue patches of pigmentation are formed without evidence of tissue reaction. Generalized argyria is recognized by the widespread pigmentation of the skin and may be seen first in the conjunctiva, with some localization in the inner canthus. Argyrosis of the respiratory tract has been described in two workers involved in the manufacture of silver nitrate; their only symptom was mild, chronic bronchitis; bronchoscopy revealed tracheobronchial pigmentation; biopsy of the nasal mucous membrane showed silver deposition in the subepithelial area. A total body burden from 1 to 5 g of silver will lead to generalized argyria. Silver, once deposited in the body, is poorly excreted in the urine in amounts detectable by spectrochemical methods. Silver nitrate (lunar caustic) may cause irritation, ulcers, and discoloration of skin; if ingested, it may cause abdominal pain and gastroenteritis.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Silver, metallic**

1. Molecular weight: 107.9
2. Boiling point (760 mm Hg): 2200 C (3992 F)
3. Specific gravity (water = 1): 10.4
4. Vapor density (air = 1 at boiling point of metallic silver): Not applicable
5. Melting point: 966 C (1771 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Silver nitrate**

1. Molecular weight: 169.9
2. Boiling point (760 mm Hg): 444 C (831 F) (decomposes)
3. Specific gravity (water = 1): 4.4
4. Vapor density (air = 1 at boiling point of silver nitrate): Not applicable
5. Melting point: 209 C (408 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): 245
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Silver fluoride**

1. Molecular weight: 126.9
2. Boiling point (760 mm Hg): 1159 C (2119 F) (approximately)
3. Specific gravity (water = 1): 5.8
4. Vapor density (air = 1 at boiling point of silver fluoride): Not applicable
5. Melting point: 435 C (815 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): 64
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of metallic silver and soluble silver compounds with acetylene may cause formation of silver acetylide that is sensitive to shock. Contact with ammonia may cause formation of compounds that are explosive when dry. Contact with strong hydrogen peroxide solutions will cause violent decomposition to oxygen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when some soluble silver compounds decompose.
4. Special precautions: Soluble silver compounds will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Most soluble silver compounds are not combustible. However, silver nitrate is a strong oxidizing material capable of increasing the flammability of combustible, organic, or other readily oxidizable materials. The following soluble silver compounds are explosives and should be stored and handled in accordance with 29 CFR 1910.109: silver acetylide, silver azide, silver fulminate, silver oxalate mixtures, silver styphnate, silver tartarate mixtures, and silver tetrazene.

• **Warning properties**

According to Stecher "many silver salts are irritating . . to mucous membranes." Grant notes that many simple silver salts and silver ammonium compounds are injurious to the eye. According to Grant, "a great many reports have been published describing argyrosis of the eye, either from local contact with silver compounds or as a part of a generalized argyrosis from systemic absorption of silver or its compounds." Since there are inadequate data to assess the effects on the eye at or near the permissible exposure limit, for the purposes of this guideline, silver metal and soluble silver compounds are 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**

An analytical method for silver metal and soluble silver

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).

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 powdered metallic silver or solids or liquids containing soluble silver compounds, where skin contact may occur.
- If employees' clothing may have become contaminated with solids or liquids containing soluble silver compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with metallic silver or soluble silver compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substances from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the substances, the person performing the operation should be informed of substances' hazardous properties.
- Non-impervious clothing which becomes contaminated with metallic silver or soluble silver compounds should be removed promptly and not reworn until the metallic silver or soluble silver compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of powdered metallic silver or solids or liquids containing soluble silver compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to silver nitrate or solutions containing 5 percent or more silver nitrate by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with metallic silver or soluble silver compounds should be promptly washed or showered to remove any metallic silver or soluble silver compounds.
- Eating and smoking should not be permitted in areas where metallic silver or solids or liquids containing soluble silver compounds are handled, processed, or stored.
- Employees who handle powdered metallic silver or solids or liquids containing soluble silver compounds 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 silver metal and soluble silver compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining and purification from ore; during refining from secondary sources	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of silver nitrate for use in photography, mirrors, plating, inks, dyes, and porcelain; and as germicides, antiseptics, caustics, and analytical reagents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of silver salts as catalysts in oxidation-reduction and polymerization reactions; in chemical synthesis; in glass manufacture, in silver-plating, in photography, as laboratory reagents, and in medicine	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Liberation from manufacture and casting of alloys; during fabrication of silver metal, alloys, and bi-metals for electrical uses; and during electroplating operations and fabrication of solders and brazing alloys; during manufacture and use of photographic chemicals and materials; during manufacture of mirrors, and during manufacture of silver powder pigments and paints	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of silver powder pigments and paints; during manufacture of mirrors; during manufacture of photographic chemicals and materials	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 powdered metallic silver or solids or liquids containing soluble silver 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 this chemical.

• **Skin Exposure**

If powdered metallic silver or solids or liquids containing soluble silver compounds get on the skin, flush the contaminated skin with water. If powdered metallic silver or solids or liquids containing soluble silver compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention. Other silver compounds should be removed by promptly flushing the skin with water.

• **Breathing**

If a person breathes in large amounts of silver metal or soluble silver 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**

If silver nitrate or other corrosive soluble silver compounds have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the silver nitrate or other corrosive silver compounds. Do not attempt to make the exposed person vomit. Get medical attention immediately. When non-corrosive soluble silver 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, 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 powdered silver metal or soluble silver compounds are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing silver metal or soluble silver compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Silver metal and soluble silver compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SILVER METAL AND SOLUBLE SILVER COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 0.01 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
20 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 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.

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

Occupational Health Guideline for Soapstone

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: 3 MgO-4SiO_2-H_2O
- Synonyms: Massive talc; steatite
- Appearance and odor: Slippery solid with no odor. (Soapstone contains less than 10% tremolite and less than 1% crystalline silica).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soapstone is 20 million particles of soapstone per cubic foot of air (mppcf) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soapstone can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Exposure to soapstone may cause scarring of the lungs. Shortness of breath, cough, enlargement of the ends of the fingers and heart failure may occur with this condition. Workers exposed to soapstone have been found to have an increased amount of cancer of the lungs and pleura.

- **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 soapstone.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soapstone 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 cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: Soapstone contains fibrous talc which can cause pneumoconiosis and lung cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Soapstone contains fibrous talc which 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**

Soapstone dust contains varying percentages of fibrous talc, which causes fibrotic pneumoconiosis and an increased incidence of cancer of the lungs and pleura. In the development of talc pneumoconiosis or talcosis, the subject initially is symptom-free, but cough and dyspnea develop as the disease progresses; cyanosis, digital clubbing, and cor pulmonale occur in advanced cases. The disease progresses slowly, even in the absence of continued exposure; occasionally, the disease may progress rapidly, with death occurring within a few years of a very heavy exposure. In an epidemiologic study of 260 workers with 15 or more years of exposure to commercial talc dust containing talc, tremolite, anthophyllite, carbonate dusts, and a small amount of free silica, the mortality rate from cancer of the lungs and pleura was four times greater than expected; in addition, a major cause of death among these workers was cor pulmonale, a result of the pneumoconiosis.

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. Formula weight: 379.2
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 2.7 – 2.8
  4. Vapor density (air = 1 at boiling point of soapstone): Not applicable
  5. Melting point: Not applicable
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

According to the *Documentation of TLV's*, "soapstone does not have a precise mineralogic connotation. Many rocks of variable composition are sometimes so designated. Massive talc is sometimes called soapstone or steatite. The terms are not synonymous, and some forms of soapstone have as little as 50% talc." Grant states that "talc employed in fulling of cloth is said to have caused conjunctival inflammation resulting in symblepharon, severe enough to require surgery in some instances."

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 soapstone 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 soapstone may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, quarrying, and blasting of soapstone	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of acid-proof coverings in floors, tables, sinks, etc.; use in switch-board panels for high electrical resistance; use in Kraft process of pulp manufacture; use in fume cupboards and fireless cookers; use in crayons for marking cloth, metal, and glass	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 soapstone 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.

- **Breathing**

If a person breathes in large amounts of soapstone, 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. Under-

stand 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 hazardous amounts of soapstone are spilled or released, 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 secured sanitary landfill.

• Waste disposal method:

Soapstone may be disposed of in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOAPSTONE

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 full facepiece and a high efficiency particulate filter.
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 Fluoride Dust (as 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.

APPLICABILITY

The general guidelines contained in this document apply to all fluoride. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Sodium fluoride

- Formula: NaF
- Synonyms: None
- Appearance and odor: Colorless or blue, odorless solid.

Cryolite (sodium hexafluoroaluminate)

- Formula: Na_3AlF_6
- Synonyms: Sodium hexafluoroaluminate
- Appearance and odor: Colorless to dark, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for fluoride is 2.5 milligrams of fluoride 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 2.5 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Inorganic Fluorides should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Fluoride 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: Fluoride containing dust may cause irritation of the eyes and respiratory tract. Swallowing fluoride may cause a salty or soapy taste, vomiting, abdominal pain, diarrhea, shortness of breath, difficulty in speaking, thirst, weakness of the pulse, disturbed color vision, muscular weakness, convulsions, loss of consciousness, and death. Kidney injury and bleeding from the stomach may occur.

2. Long-term Exposure: Repeated exposure to fluoride containing dust may cause excessive calcification of the bone and calcification of ligaments of the ribs, pelvis, and spinal column. Stiffness and limitation of motion may result. Repeated or prolonged exposure of the skin to fluoride containing dust 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 fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 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 disease interferes with excretion of fluoride, thus increasing the risk from exposure to excessive fluoride, a urinalysis should 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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obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic examination on centrifuged sediment. An analysis for fluoride should be performed.

—Pelvic roentgenogram: Fluoride causes 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 fluoride tests.

—Eye disease: Fluoride is an 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: Fluoride may cause respiratory system effects, such as fibrosis and asthma. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Fluoride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Fluoride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that the radiologic examination of the pelvis should be conducted only when clinically indicated.

- **Summary of toxicology**

Fluoride causes irritation of the eyes and respiratory tract; absorption of excessive amounts of fluoride over a long period of time results in increased radiographic density of bone. The lethal oral dose of sodium fluoride for humans is approximately 5 g; effects are diffuse abdominal pain, diarrhea, and vomiting; excessive salivation, thirst, and perspiration; painful spasms of the limbs; and sometimes albuminuria. Workers exposed to an airborne fluoride concentration of 5 mg/m^3 complained of eye and respiratory tract irritation and nausea. A portion of absorbed fluoride is stored in bone and part is excreted promptly in the urine; with continued exposure and increasing amounts of fluoride already present in the bone, the fraction appearing in the urine increases. Some storage of fluoride occurs from the ingestion of as little as 3 mg/day. Repeated exposure to excessive concentrations of fluorides over a period of years results in increased radiographic density of bone and eventually may cause crippling fluorosis (osteosclerosis due to deposition of fluoride). The gross changes in the skeleton are quite distinctive and characteristic; as the amount of fluoride in the bone increases, exostoses may develop, especially on the long bones; the spinal and pelvic ligaments begin to calcify, occasionally vertebrae fuse together, and a typical stiffness of the spinal column develops. The absorption of 20 to 80 mg of fluoride daily may be expected to lead to crippling fluorosis in 10 to 20 years; this condition has not been reported in the United States from industrial exposure. Evidence from several sources indicates that urinary fluoride concentrations not exceeding 5 mg/l in preshift samples taken after 2 days off work are not associated with detectable osteosclerosis and that such changes are unlikely at urinary levels of 5 to 8 mg/l. Repeated or prolonged exposure of the skin to fluoride-bearing dusts and fumes may cause dermatitis. Mottled appearance and altered form of teeth are most pronounced when excessive amounts of fluoride are ingested during the period of formation and calcification of teeth, which occurs during the first 8 years of life in humans; after the teeth erupt and calcification has been completed, fluoride does not have an adverse effect on the teeth.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Sodium fluoride**
  1. Molecular weight: 42
  2. Boiling point (760 mm Hg): 1702 C (3095 F)
  3. Specific gravity (water = 1): 2.8
  4. Vapor density (air = 1 at boiling point of sodium fluoride): Not applicable
  5. Melting point: 992 C (1818 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 4.2
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Cryolite (sodium hexafluoroaluminate)**
  1. Molecular weight: 209.9
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 2.8
  4. Vapor density (air = 1 at boiling point of cryolite): Not applicable
  5. Melting point: 1009 C (1848 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.04
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with strong acids may cause formation of toxic and irritating hydrogen fluoride gas.
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Concerning fluorides, Grant states that "industrially, fluorides may contact the eyes in the form of fumes from fluxes in soldering, in welding, and in magnesium foundries. Irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m^3 of air."

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 fluoride in an impinger containing sodium hydroxide, followed by dilution with a buffer, and analysis with an ion-specific electrode. An analytical method for fluoride is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with fluoride.

• If employees' clothing has had any possibility of being contaminated with fluoride, employees should change into uncontaminated clothing before leaving the work premises.

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

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of sodium fluoride or liquids containing sodium fluoride contacting the eyes.

• Non-impervious clothing which becomes contaminated with fluoride should be removed promptly and not reworn until the fluoride is removed from the clothing.

SANITATION

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

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

• Employees who handle fluoride 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 fluoride dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, benefication, packaging, and distribution of fluorspar	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from fluorides from phosphate rock treatment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from use of fluorspars as a fluxing additive for steel production	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from manufacture of cryolite from phosphate rock processing; use of fluorspar and cryolite in the production of metallic aluminum by electrolysis	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in formulations of insecticides for agricultural crops, fruits, vegetables, ornamentals, and trees	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in chemical industry as a source of fluorine compounds; use of fluorspar and cryolite in ceramics and glass industry in manufacture of fiberglass, optical glass, lenses, and pottery; use of fluorspar in manufacture of welding rods and welding fluxes; use in electroplating	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in treatment of water	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 fluoride or liquids containing fluoride 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 fluoride or liquids containing fluoride get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If fluoride or liquids containing fluoride 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 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**

When liquids containing fluoride 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 or releases until cleanup has been completed.
- If fluoride 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 and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing fluoride should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Fluoride may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR FLUORIDE DUST (AS FLUORIDE)

Condition	Minimum Respiratory Protection* Required Above 2.5 mg/m³
Particulate Concentration	
12.5 mg/m³ or less**	A single-use dust respirator.
25 mg/m³ or less**	Any dust respirator, except single-use or quarter-mask respirator.***
	Any supplied-air respirator.
	Any self-contained breathing apparatus.
125 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece.***
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
250 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter, and 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 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	An escape gas mask with an acid gas canister.
	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.

***If acid gases are present, air-purifying elements providing protection against acid gases and including the indicated filters should be used.

Occupational Health Guideline for Sodium Fluoroacetate

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: $CH_2FCOONa$
- Synonyms: 1080; sodium monofluoroacetate; SFA
- Appearance and odor: Fluffy, white, odorless hygroscopic solid (sometimes dyed black).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sodium fluoroacetate is 0.05 milligram of sodium fluoroacetate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sodium fluoroacetate 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**

Sodium fluoroacetate may cause vomiting, apprehension, hallucinations, tingling of the nose and face, numbness of the face and facial twitching. It may also cause excitation and convulsions. Depression may occur after and between convulsive episodes. The heart may beat irregularly or stop. Symptoms are often delayed 30 minutes to two hours after swallowing 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 sodium fluoroacetate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sodium fluoroacetate 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 or cardiovascular disease would be expected to be at increased risk from exposures. Examination of the nervous system, heart, lungs, and kidneys should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to sodium fluoroacetate, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—An electrocardiogram: Sodium fluoroacetate causes cardiac arrhythmias. Periodic surveillance of the heart is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Sodium fluoroacetate as the dust or in solution is highly toxic and causes convulsions and ventricular fibrillation. Fluoroacetate is metabolized to fluorocitrate, which blocks the tricarboxylic acid cycle, an essential element of energy production in mammalian cells. Estimates of the lethal oral dose in humans range from 2 to 10 mg/kg. Onset of symptoms after ingestion is frequently delayed for 30 minutes to 2 hours; effects are vomiting, apprehension, auditory hallucinations, nystagmus, tingling sensation of nose, numbness of face, facial twitching, and epileptiform convulsions. After a period of several hours there may be pulsus alternans, long sequences of ectopic heartbeats (often multifocal), tachycardia, ventricular fibrillation, and death. In a fatal

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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case of ingestion, autopsy findings included hemorrhagic pulmonary edema and degeneration of renal tubules.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 100
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): Greater than 1
  4. Vapor density (air = 1 at boiling point of sodium fluoroacetate): Not applicable
  5. Melting point: 200 C (392 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 111
  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 fluoride and carbon monoxide) may be released when sodium fluoroacetate decomposes.
  4. Special precautions: None.
- **Flammability**
  1. Not combustible
- **Warning properties**

Sodium fluoroacetate is not known to be an eye irritant. Grant describes some effects on the eye caused by this compound, but these are systemic effects.

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 sodium fluoroacetate 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 sodium fluoroacetate or solutions containing sodium fluoroacetate.
- If employees' clothing has had any possibility of being contaminated with sodium fluoroacetate or solutions containing sodium fluoroacetate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with sodium fluoroacetate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sodium fluoroacetate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sodium fluoroacetate, the person performing the operation should be informed of sodium fluoroacetate's hazardous properties.
- Where there is any possibility of exposure of an employee's body to sodium fluoroacetate or solutions containing sodium fluoroacetate, 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 sodium fluoroacetate should be removed immediately and not reworn until the sodium fluoroacetate is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium fluoroacetate or solutions containing sodium fluoroacetate may contact the eyes.

SANITATION

- Skin that becomes contaminated with sodium fluoroacetate should be immediately washed or showered to remove any sodium fluoroacetate.
- Workers subject to skin contact with sodium fluoroacetate or solutions containing sodium fluoroacetate should wash any areas of the body which may have contacted sodium fluoroacetate at the end of each work

day.

• Eating and smoking should not be permitted in areas where sodium fluoroacetate or solutions containing sodium fluoroacetate are handled, processed, or stored.

• Employees who handle sodium fluoroacetate or solutions containing sodium fluoroacetate 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 sodium fluoroacetate may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of pesticides	Local exhaust ventilation; personal protective equipment
Use in hand or aircraft application for pest control	Personal protective equipment; material substitution (product replacement)
Manufacture of sodium fluoroacetate	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 sodium fluoroacetate or solutions containing sodium fluoroacetate 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 sodium fluoroacetate or solutions containing sodium fluoroacetate get on the skin, immediately flush the contaminated skin with water. If sodium fluoroacetate or solutions containing sodium fluoroacetate penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation is present after washing, get medical attention promptly.

• **Breathing**

If a person breathes in large amounts of sodium fluoroacetate, 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 sodium fluoroacetate or solutions containing sodium fluoroacetate 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 sodium fluoroacetate 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 sodium fluoroacetate should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Sodium fluoroacetate may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SODIUM FLUOROACETATE

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m³
Particulate Concentration	
0.25 mg/m³ or less	Any dust and mist respirator, except single-use.
0.5 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
2.5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5 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 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 Sodium Hydroxide

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: NaOH
- Synonyms: Caustic soda, soda lye, lye
- Appearance and odor: White, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sodium hydroxide is 2 milligrams of sodium hydroxide 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 a ceiling of 2 mg/m^3 over a 15-minute period. The NIOSH Criteria Document for Sodium Hydroxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sodium hydroxide 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**

Sodium hydroxide is a strong alkali and is corrosive to any tissue with which it comes in contact. Effects from inhalation of the dusts and mists will vary from mild irritation to destructive burns depending on the severity of exposure. Severe pneumonitis may occur. Sodium hydroxide as a solid or in dusts, mists or solutions may cause irritation of the eyes and, with greater exposure, severe burns with possible blindness. Contact of the skin with sodium hydroxide as a solid or in dusts, mists or solutions may cause skin irritation and, with greater exposure, severe burns with scarring. Swallowing solid sodium hydroxide or solutions of sodium hydroxide may cause severe burns of the mouth, throat, and stomach. Death may result. Severe scarring of the throat may occur on recovery after swallowing sodium hydroxide. An increased number of esophageal cancer cases have been reported to occur in individuals who have scarring of the esophagus from swallowing sodium hydroxide.

- **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 sodium hydroxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sodium hydroxide 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 respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Sodium hydroxide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sodium hydroxide 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**

Sodium hydroxide is a strong alkali; the mist, dust and solutions cause severe injury to the eyes, mucous mem-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Safety and Health Administration

branes, and skin. Although inhalation is usually of secondary importance in industrial exposures, the effects from the dust or mist will vary from mild irritation of the nose at 2 mg/m^3 to severe pneumonitis, depending on the severity of exposure. The greatest industrial hazard is rapid tissue destruction of eyes or skin upon contact with either the solid or with concentrated solutions. Contact with the eyes causes disintegration and sloughing of conjunctival and corneal epithelium, corneal opacification, marked edema, and ulceration; after 7 to 13 days either gradual recovery begins, or there is progression of ulceration and corneal opacification. Complications of severe eye burns are symblepharon (adhesion of the lid to the eyeball) with overgrowth of the cornea by a vascularized membrane, progressive or recurrent corneal ulceration, and permanent corneal opacification. On the skin, solutions of 25 to 50% cause the sensation of irritation within about 3 minutes; with solutions of 4%, this does not occur until after several hours. If not removed from the skin, severe burns with deep ulceration will occur; exposure to the dust or mist may cause multiple small burns, with temporary loss of hair. Ingestion produces severe pain in the esophagus and stomach, corrosion of the lips, mouth, tongue, and pharynx and the vomiting of large pieces of mucosa; cases of squamous cell carcinoma of the esophagus have occurred with latent periods of 12 to 42 years after ingestion; these cancers may have been sequelae of tissue destruction and possibly scar formation rather than from a direct carcinogenic action of sodium hydroxide itself.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 40
  2. Boiling point (760 mm Hg): 1390 C (2534 F)
  3. Specific gravity (water = 1): 2.13
  4. Vapor density (air = 1 at boiling point of sodium hydroxide): Not applicable
  5. Melting point: 310 C (590 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 50
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with water, acids, flammable liquids, and organic halogen compounds, especially trichloroethylene, may cause fires and explosions. Contact with metals such as aluminum, tin, and zinc causes formation of flammable hydrogen gas. Contact with nitromethane and other similar nitro compounds causes formation of shock-sensitive salts.
  3. Hazardous decomposition products: None
  4. Special precautions: Sodium hydroxide will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

Grant states that sodium hydroxide "is severely injurious to all tissues, and causes some of the most severe injuries of the eye. The serious problem presented by sodium hydroxide and other alkalies which cause devastating injuries of the eye have been succinctly and well described by Stanley, emphasizing particularly the dangers of caustic household drain cleaners that contain sodium hydroxide.

"The effects of splashes of sodium hydroxide on the eyes of human beings have been described innumerable times . . . . Damage of the cornea, conjunctiva, and episcleral tissues is usual, but damage of intraocular structures is relatively rare."

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 sodium hydroxide. 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 sodium hydroxide in a glass bubbler containing hydrochloric acid, followed by subsequent titration. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sodium hydroxide may be used. An analytical method for sodium hydroxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental

concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with sodium hydroxide or solutions of sodium hydroxide.
- If employees' clothing may have become contaminated with solid sodium hydroxide, employees should change into uncontaminated clothing before leaving the work premises.
- Where there is any possibility of exposure of an employee's body to sodium hydroxide or solutions of sodium hydroxide, 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 sodium hydroxide should be removed immediately and not reworn until the sodium hydroxide is removed from the clothing.
- Clothing contaminated with sodium hydroxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sodium hydroxide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sodium hydroxide, the person performing the operation should be informed of sodium hydroxide's hazardous properties.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of sodium hydroxide or solutions of sodium hydroxide contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to sodium hydroxide or solutions of sodium hydroxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with sodium hydroxide should be immediately washed or showered to remove any sodium hydroxide.
- Eating and smoking should not be permitted in areas where sodium hydroxide or solutions containing sodium hydroxide are stored.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in chemical manufacture; explosives manufacture; use in boiler water and as a laboratory reagent; use in pH control in textiles, paper, and chemical industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of synthetic fibers and plastics	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of pulp and paper; in pulping Kraft process; manufacture of insulating board	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in metal processing and refining; use in petroleum refining for removal of sulfur compounds; as a flotation reagent; as a modifier and slime depressant; in pH control	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of soaps and detergents; as a saponifying agent; use in metal cleaning; in laundering, bleaching, and dishwashing; use in drain cleaners and oven cleaners	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in food processing to peel fruits and vegetables, process olives, and refine vegetable oils	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Use in glass manufacture as a source of sodium oxide	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 sodium hydroxide, as a solid or in dusts, mists, or solutions, 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 sodium hydroxide, as a solid or in dusts, mists, or solutions, gets on the skin, immediately flush the contaminated skin with water. If sodium hydroxide, as a solid or in dusts, mists, or solutions, penetrates 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 sodium hydroxide, 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 sodium hydroxide have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the sodium hydroxide. 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 sodium hydroxide is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Dilute with water and neutralize with 6 molar hydrochloric acid.

• Waste disposal method:

Sodium hydroxide may be disposed of in sealed containers in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on sodium hydroxide, look up sodium hydroxide in the following documents:

• Medical Surveillance for Chemical Hazards
• Respiratory Protection for Chemical Hazards
• Personal Protection and Sanitation for Chemical Hazards
• NIOSH Criteria Document for Sodium Hydroxide (September 1975)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR SODIUM HYDROXIDE

Condition	Minimum Respiratory Protection* Required Above 2 mg/m³
Particulate Concentration	
100 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 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 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 with a full facepiece, except single-use. 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 sodium hydroxide; 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 Stibine

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: SbH_3
- Synonyms: Hydrogen antimonide; antimony trihydride
- Appearance and odor: Colorless gas with a disagreeable odor like hydrogen sulfide.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for stibine is 0.1 part of stibine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.5 milligram of stibine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Stibine can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Stibine may cause destruction of the red blood cells with headache, nausea, weakness, and back and abdominal pain. It may later cause dark red urine, yellow jaundice, kidney damage, and death. It may also cause lung irritation.

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 stibine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to stibine 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 kidneys should be stressed.

—A complete blood count: Stibine causes red blood cell hemolysis. 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 stibine, 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 stibine, 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**

Stibine gas is an extremely toxic hemolytic agent which causes injury to the liver and kidneys; it also may be a lung irritant. Guinea pigs exposed to 65 ppm for 1 hour developed hemoglobinuria, followed within a few days by profound anemia. Cats and dogs exposed to 40-45 ppm for 1 hour developed pulmonary edema, and some died within 24 hours. Acute exposures to humans would be expected to cause rapid destruction of red blood cells, hemoglobinuria, anuria, jaundice, and death. Workers exposed to a mixture of gases of stibine, arsine, and hydrogen sulfide developed headache, weakness, nausea, abdominal and lumbar pain, hematuria, and profound anemia.

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: 124.8
  2. Boiling point (760 mm Hg): −17 C (1 F)
  3. Specific gravity (water = 1): Liquid = 2.2 at boiling point
  4. Vapor density (air = 1 at boiling point of stibine): 4.34
  5. Melting point: −88 C (−126 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): 0.1
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Stibine reacts with acids, halogenated hydrocarbons, oxidizers, and moisture.
  3. Hazardous decomposition products: Antimony and hydrogen will be released when stibine dcomposes.
  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: Stop flow of gas.
- **Warning properties**
  1. Odor Threshold: Patty states that "stibine has an extremely unpleasant odor that can serve as a warning; whether the threshold of odor detection is sufficiently low to prevent injury is uncertain." No quantitative information is available concerning the odor threshold of stibine.
  2. Eye Irritation Level: Stibine is not known to be an eye irritant.
  3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of stibine, 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**

Sampling and analyses may be performed by collection of stibine on mercuric chloride-impregnated silica gel, followed by extraction with concentrated hydrochloric acid, and colorimetric analysis. An analytical method for stibine 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 stibine may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from treatment of scum formed on surface of molten metals treated with acid	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation during charging as storage batteries	Local exhaust ventilation; general dilution ventilation
Liberation from alloys of antimony compounds which come in contact with reducing acids	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation from purification of antimony by electrolysis	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a chemical intermediate and in chemical synthesis	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.

• **Breathing**

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

1. Ventilate area of leak to disperse gas.
2. Control source of stibine formation.

REFERENCES

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

• American Industrial Hygiene Association: "Stibine," *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 STIBINE

Condition	Minimum Respiratory Protection* Required Above 0.1 ppm
Gas Concentration	
1 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against stibine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Stoddard Solvent

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: Generally C_9 through C_{11} paraffins (85%) and aromatics (15%)
- Synonyms: Dry cleaning safety solvent; mineral spirits
- Appearance and odor: Colorless liquid with kerosene-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for Stoddard solvent is 500 parts of Stoddard solvent per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2950 milligrams of Stoddard solvent per cubic meter of air (mg/m³). NIOSH has recommended that the permissible exposure limit for refined petroleum products, including Stoddard solvent, be reduced to 350 mg/m³ averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 1800 mg/m³ measured over a 15-minute period. The NIOSH Criteria Document for Refined Petroleum Products should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Stoddard solvent 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 Stoddard solvent causes irritation of the eyes, nose, and throat, and may cause dizziness. Very high air concentrations may cause unconsciousness and death.

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 Stoddard solvent.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to Stoddard solvent 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, blood, urine, and central nervous system should be stressed.

—Skin: Stoddard solvent 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 function tests: Stoddard Solvent may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Urinalysis: The kidneys may be affected by Stoddard solvent. 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.

—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.

—Respiratory system examination: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of Stoddard solvent might cause exacerbation of symptoms due to its irritant properties.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, tney 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.

• **Summary of toxicology**

Stoddard solvent vapor is a mild narcotic and a mucous membrane irritant. Since it contains both aliphatic and aromatic hydrocarbons in varying concentrations, toxicologic opinion is based upon deductions as to the relative health hazard of the different fractions. The vapor of the aliphatic fractions is chiefly nonane and isodecane. The aromatic component is considered to be more toxic. Stoddard solvent has an odor threshold of about 4 to 5 mg/m^3 and olfactory fatigue has been observed in about 6 minutes at low concentrations. Eye irritation was reported in a test exposure of human subjects at 850 mg/m^3. Industrial exposures to unknown but fairly high concentrations over long periods have resulted in headaches, eye, nose, and throat irritation, fatigue, marrow hypoplasia and, in extreme cases, death. Dermal exposures to the liquid solvent have caused dermatitis and jaundice.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 144 (approximately)
2. Boiling point (760 mm Hg): 150 to 200 C (302 to 392 F)
3. Specific gravity (water = 1): 0.78
4. Vapor density (air = 1 at boiling point of Stoddard solvent): 5
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 2 mm Hg (estimate)
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 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 Stoddard solvent.
4. Special precautions: Stoddard solvent will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 38.7 to 60 C (102 to 140 F) (closed cup)
2. Autoignition temperature: 226 to 260 C (440 to 500 F)
3. Flammable limits in air, % by volume: Lower: 0.8
4. Extinguishant: Carbon dioxide, dry chemical, foam

• **Warning properties**

1. Odor Threshold: May gives an odor threshold of 30 ppm for Stoddard solvent (mineral spirits). According to the AIHA *Hygienic Guide* for Stoddard solvent, "most Stoddard solvents have a petroleum odor that is perceptible at about 1 ppm."
2. Eye Irritation Level: Grant states that "the vapor of Stoddard solvent is perceptively irritating to human eyes at 400 ppm."
3. Evaluation of Warning Properties: Through its odor and irritant effects, Stoddard solvent can be detected below the permissible exposure limit. For the purposes of this guideline, therefore, Stoddard solvent 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 Stoddard solvent. 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 Stoddard solvent 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 Stoddard solvent may be used. An analytical method for Stoddard solvent 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 Stoddard solvent.

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

• Any clothing which becomes wet with liquid Stoddard solvent should be removed promptly and not reworn until the Stoddard solvent is removed from the clothing.

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

SANITATION

• Skin that becomes wet with liquid Stoddard solvent should be promptly washed or showered with soap or mild detergent and water to remove any Stoddard solvent.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as a solvent in dry cleaning industry	Process enclosure; local exhaust ventilation; personal protective equipment
Use in paint and varnish industries	General dilution ventilation
Use as a solvent for printing inks and textile-printing industries	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of aerosol sprays as a solvent for paints, varnishes, and insecticides	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of sprays for pesticides, herbicides, household cleaners, and silicone compounds	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent and thinner in protective coating materials	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in metal cleaning and degreasing; and in leather degreasing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a general solvent in fabric water-proofing, processing of synthetic yarns, extraction of fats and oils, as a tackifying agent for rubber, in rubber cements, and in polishes	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 Stoddard solvent 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 Stoddard solvent gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If Stoddard solvent 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 Stoddard solvent, 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 Stoddard solvent 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 Stoddard solvent 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. Stoddard solvent should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Stoddard solvent 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: "Stoddard Solvent," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

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• 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 STODDARD SOLVENT

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 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 Strychnine

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: $C_{21}H_{22}N_2O_2$
- Synonyms: None
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for strychnine is 0.15 milligram of strychnine per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Strychnine affects the body after it is swallowed. There are no literature sources to indicate that strychnine presents a significant hazard from skin or eye exposure.

- **Effects of overexposure**

After swallowing strychnine, effects usually occur within 10 to 30 minutes and include stiffness of the face and neck muscles, increased excitability, restlessness, and apprehension. These symptoms may progress to repeated convulsions 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 strychnine.

- **Recommended medical surveillance**

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

—Convulsive disorders: Strychnine causes convulsions. Persons with a history of convulsive 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**

Strychnine is a potent convulsant. In humans the mean lethal oral dose is approximately 100 to 120 mg. After ingestion, effects usually occur within 10 to 30 minutes and include stiffness of the face and neck muscles, increased reflex excitability, restlessness, apprehension, and heightened acuity of perception. Any sensory stimulus may produce a violent motor response which in the early stages of intoxication tends to be a coordinated extensor thrust and in later stages it may be a tetanic convulsion with opisthotonos; anoxia and cyanosis develop rapidly. Between convulsions, muscular relaxation is complete, breathing is resumed, and cyanosis lessens. Because sensation is unaffected, the convulsions are painful and lead to overwhelming fear; as many as 10 convulsions separated by intervals of 10 to 15 minutes may be experienced, but death often occurs after the second to fifth convulsion and even the first convulsion may be fatal if sustained; death is commonly due to asphyxia.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 334.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.36
4. Vapor density (air = 1 at boiling point of strychnine): Not applicable
5. Melting point: 268 C (547 F)
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): 0.02

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 nitrogen and carbon monoxide) may be released when strychnine decomposes.

4. Special precautions: None.

• **Flammability**

1. Not combustible

• **Warning properties**

Strychnine 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 strychnine 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

• If employees' clothing has had any possibility of being contaminated with strychnine or liquids containing strychnine, employees should change into uncontaminated clothing before leaving the work premises.

• 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 strychnine where skin contact may occur.

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

SANITATION

• Eating and smoking should not be permitted in areas where strychnine or liquids containing strychnine are handled, processed, or stored.

• Skin that becomes contaminated with strychnine or liquids containing strychnine should be promptly washed or showered to remove any strychnine.

• Employees who handle strychnine or liquids containing strychnine 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 strychnine may occur and control methods which may be effective in each case:

Operation	Controls
Application and formulation of medicinals and pesticides	Personal protective equipment
Manufacture of strychnine	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 strychnine or liquids containing strychnine get 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 strychnine or liquids containing strychnine get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If strychnine or liquids containing strychnine 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 strychnine, 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 strychnine or liquids containing strychnine 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 strychnine 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 strychnine should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Strychnine may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR STRYCHNINE

Condition	Minimum Respiratory Protection* Required Above 0.15 mg/m³
Particulate Concentration	
0.75 mg/m³ or less	Any dust respirator, except single-use.
1.5 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.
3 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. A powered air-purifying respirator with a high efficiency particulate filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 3 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for 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: $C_6H_5CH=CH_2$
- Synonyms: Phenylethylene; vinylbenzene; cinnamene; styrene monomer
- Appearance and odor: Colorless liquid with a sweet aromatic odor at low concentrations. Sharp, penetrating, and disagreeable odor at higher concentrations.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for styrene is 100 parts of styrene per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and an acceptable peak of 600 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 styrene from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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: Styrene may irritate the eyes, nose, throat, and skin. High concentrations may cause a person to become sleepy or to become unconscious.
2. Long-term Exposure: Repeated skin contact with styrene may produce 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 styrene.

- **Recommended medical surveillance**

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

—Central nervous system disorders: Since exposure to styrene vapor or liquid on the skin has been observed to result in central nervous system depression and occasional abnormalities in the electroencephalogram, persons with pre-existing disorders may be unusually susceptible to these effects.

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

—Skin disease: Styrene 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 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 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**

Exposure to concentrations of styrene above 200 ppm

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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causes irritation of the eyes and upper respiratory tract. There is cracking and inflammation of the skin due to defatting. Higher exposures depress the central nervous system. Electroencephalographic changes have been reported. Styrene is excreted fairly rapidly in the urine, largely as hippuric acid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 104
  2. Boiling point (760 mm Hg): 145 C (293 F)
  3. Specific gravity (water = 1): 0.90
  4. Vapor density (air = 1 at boiling point of styrene): 3.6
  5. Melting point: −30.6 C (−23 F)
  6. Vapor pressure at 20 C (68 F): 4.5 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.03
  8. Evaporation rate (butyl acetate = 1): 0.49
- **Reactivity**

1. Conditions contributing to instability: Styrene is stabilized by a polymerization inhibitor (often tert-butylcatechol). If this is not present in adequate concentrations, styrene can polymerize and explode its container. The polymerization is also speeded up by temperatures above 66 C (150 F).

2. Incompatibilities: Avoid contact with oxidizing agents and catalysts for vinyl polymerization, such as peroxides, strong acids, and aluminum chloride.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving styrene. Styrene fumes are very acrid.

4. Special precautions: Styrene will corrode copper and copper alloys and dissolve rubber.

- **Flammability**
  1. Flash point: 32 C (90 F) (closed cup)
  2. Autoignition temperature: 490 C (914 F)
  3. Flammable limits in air, % by volume: Lower: 1.1; Upper: 6.1
  4. Extinguishant: Dry cemical, foam, or carbon dioxide
- **Warning properties**

1. Odor Threshold: May reports that the odor threshold of styrene is 0.08 ppm.

2. Eye Irritation Level: The AIHA *Hygienic Guide* reports that "styrene vapor at concentrations of 200 to 400 ppm was found to have transient irritant effects on the eyes."

4. Evaluation of Warning Properties: Since the odor threshold of styrene is below 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 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.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of styrene. 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 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 styrene may be used. An analytical method for 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 styrene.
- Clothing wet with liquid styrene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of styrene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the styrene, the person performing the operation should be informed of styrene's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid styrene should be removed promptly and not reworn until the styrene is removed from the clothing.
- Any clothing which becomes wet with liquid styrene should be removed immediately and not reworn until the styrene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid styrene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid styrene should be promptly washed or showered with soap or mild detergent and water to remove any styrene.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during spray-up manufacture of glass fiber, reinforced styrene-polyester articles	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during spray application of styrene polyester surface coatings	Process enclosure; local exhaust ventilation; personal protective equipment
Use during hand lay-up of glass fibers, reinforced styrene-polyester articles	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during molding of articles or potting electrical components with polystyrene	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of tires and other rubber goods using styrene-butadiene elastomers (SBR)	General dilution ventilation
Use in manufacture of concretes	General dilution ventilation; personal protective equipment
Use during bag lay-up manufacture of glass fiber, reinforced styrene-polyester articles; during use of surface coatings containing styrene-butadiene copolymer resins	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during die molding of articles made from styrene-polyester resins; during brush application of surface coatings	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in process operations for production of polystyrene, acrylonitrile-butadiene styrene (ABS), styrene-acrylonitrile (SAN), and styrene-butadiene copolymers	Local exhaust ventilation; personal protective equipment
Use in manufacture of surface coatings; use in miscellaneous processes as an elastomer, intermediate, or starting material; use during manufacture of ion-exchange resins (styrene-divinylbenzene copolymer)	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 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 styrene gets on the skin, promptly flush the contaminated skin with water. If 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 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 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 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 more flammable liquid.

• Waste disposal methods:

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 more flammable liquid.

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RESPIRATORY PROTECTION FOR STYRENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
400 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).
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.

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

Occupational Health Guideline for Sulfur 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: SO_2
- Synonyms: None
- Appearance and odor: Colorless gas with a characteristic pungent odor. It can be a liquid at temperatures below – 10 C (14 F).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfur dioxide is 5 parts of sulfur dioxide per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 13 milligrams of sulfur dioxide per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 0.5 ppm as a time-weighted average for up to a 10-hour work shift, 40-hour work week. For more detailed information, the NIOSH Criteria Document for Sulfur Dioxide and the NIOSH testimony presented at the Department of Labor's Public Hearing on a Proposed Standard for Sulfur Dioxide should be consulted.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfur dioxide can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

- **Effects of overexposure**

Sulfur dioxide gas is intensely irritating to the eyes and respiratory tract causing burning of the eyes and tearing, coughing, and chest tightness. It may cause severe breathing difficulties. Severe exposures to sulfur dioxide may cause a person to stop breathing. Liquid sulfur dioxide may cause eye burns with loss of vision and skin burns.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfur dioxide.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfur 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 eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Sulfur dioxide causes human lung irritation. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfur dioxide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Sulfur dioxide gas is a severe irritant of the eyes, mucous membranes, and skin. Its irritant properties are due to the rapidity with which it forms sulfurous acid on contact with moist membranes. In combination with certain particulate matter and/or oxidants, the effects may be markedly increased. Approximately 90% of all sulfur dioxide inhaled is absorbed in the upper respiratory passages, where most effects occur; however, high concentrations may produce respiratory paralysis and pulmonary edema. Exposure to concentrations of 10 to 50 ppm for 5 to 15 minutes causes irritation of the eyes,

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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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nose, and throat, rhinorrhea, choking, cough, and, in some instances, reflex bronchoconstriction with increased pulmonary resistance. Some 10 to 20% of the healthy young adult population is estimated to be hypersusceptible to the effects of sulfur dioxide, while the phenomenon of adaptation to irritating concentrations is a recognized occurrence in experienced workers. Workers repeatedly exposed to 10 ppm experienced upper respiratory irritation and some nosebleeds, but the symptoms did not occur at 5 ppm; in another study, initial cough and irritation did occur at 5 ppm and 13 ppm, but subsided after 5 minutes of exposure. In a human experimental study with the subjects breathing through the mouth, brief exposure to 13 ppm caused a 73% increase in pulmonary flow resistance; 5 ppm resulted in a 40% increase; 1 ppm produced no effects. Exposure of the eyes to liquid sulfur dioxide from pressurized containers causes corneal burns and opacification resulting in a loss of vision. The liquid on the skin produces skin burns from the freezing effect of rapid evaporation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 64.1
2. Boiling point (760 mm Hg): −10 C (14 F)
3. Specific gravity (water = 1): 1.46 (liquid)
4. Vapor density (air = 1 at boiling point of sulfur dioxide): 2.26
5. Melting point: −75.5 C (−104 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): 10
8. Evaporation rate (butyl acetate = 1): Much greater than 1

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
2. Incompatibilities: Contact with some powdered metals and with alkali metals such as sodium or potassium may cause fires and explosions.
3. Hazardous decomposition products: None.
4. Special precautions: Liquid sulfur dioxide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible
2. Compressed gas cylinders containing sulfur dioxide should be stored in accordance with 29 CFR 1910.101.

- **Warning properties**

1. Odor Threshold: The *Documentation of TLV's* reports that "Henderson and Haggard gave the odor threshold as 3 to 5 ppm."
2. Eye Irritation Level: Patty states that "20 ppm is the least amount irritating to the eyes."
3. Other Information: Patty states that "sulfur dioxide is an irritant gas: 6 to 12 ppm causes immediate irritation to nose and throat. Three tenths to 1 ppm can be detected by the average individual, probably by taste rather than by odor, and 3 ppm has an easily noticeable odor."
4. Evaluation of Warning Properties: Through odor and taste, sulfur dioxide can be detected at or below the permissible exposure limit. Nose and throat irritation occur within three times the permissible exposure limit. For the purposes of this guideline, therefore, sulfur dioxide 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 gas in a hydrogen peroxide-filled impinger with a subsequent chemical analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sulfur dioxide may be used. An analytical method for sulfur dioxide 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 sulfur dioxide or from contact with vessels containing liquid sulfur dioxide.

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

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid sulfur dioxide contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid sulfur dioxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as bleaching and preservative agent in wood and pulp, sugar and food preparation industries; as a selective antiseptic in food industry and as a fumigating agent in ships	Process enclosure and/ or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as solvent in oil refineries; during synthesis in chemical, petroleum, textile, pharmaceutical, tanning, photography, metal, and rubber industries	Process enclosure and/ or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as refrigerant in commercial refrigerators	Process enclosure and/ or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during extraction, enrichment, and recovery processes in mining and metallurgy industry	Process enclosure and/ or local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous processes during leather tanning, special glass manufacture, water treatment, textile processing, and chrome waste treatment	Process enclosure and/ or 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 sulfur dioxide or strong concentrations of sulfur dioxide 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 sulfur dioxide gets on the skin, immediately flush the contaminated skin with water. If liquid sulfur dioxide 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 sulfur dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

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 sulfur dioxide is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in liquid form, allow to vaporize.

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RESPIRATORY PROTECTION FOR SULFUR DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
20 ppm or less	Any chemical cartridge respirator with a cartridge(s) providing protection against sulfur dioxide.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
100 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against sulfur dioxide. A gas mask with a chin-style or a front- or back-mounted canister providing protection against sulfur dioxide. 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 sulfur dioxide. 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 Sulfuric 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: H_2SO_4
- Synonyms: Oil of vitriol
- Appearance and odor: Colorless to dark brown, oily, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfuric acid is 1 milligram of sulfuric acid per cubic meter of air (mg/m³) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 1 mg/m³ averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Sulfuric Acid should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfuric 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: Sulfuric acid may cause irritation of the eyes, nose, and throat. Breathing in the mist or vapor may cause teeth erosion or the mouth to become sore and also difficulty in breathing. Splashes in the eyes or on the skin will cause severe skin burns.
2. Long-term Exposure: Repeated or prolonged exposure to dilute solutions of sulfuric acid may cause irritation of the skin. Repeated or prolonged exposure to mists or vapors of sulfuric acid may cause erosion of the teeth, chronic irritation of the eyes, or chronic inflammation 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 sulfuric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfuric 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 respiratory system, eyes, and teeth should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Sulfuric acid may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfuric acid is reported to cause pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Sulfuric acid mist severely irritates the eyes, respiratory tract, and skin. Concentrated sulfuric acid destroys tissue due to its severe dehydrating action, whereas the dilute form acts as a milder irritant due to acid properties. The LC50 of mist of 1-micron particle size for an 8 hour exposure was 50 mg/m³ for adult guinea pigs and 18 mg/m³ for young animals. Continuous exposure of guinea pigs to 2 mg/m³ for 5 days caused pulmonary edema and thickening of the alveolar walls; exposure of guinea pigs to 2 mg/m³ for 1 hour caused an increase in

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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

September 1978

pulmonary airway resistance from reflex bronchoconstriction. A worker sprayed in the face with liquid fuming sulfuric acid suffered skin burns of the face and body, as well as pulmonary edema from inhalation. Sequelae were pulmonary fibrosis, residual bronchitis, and pulmonary emphysema; in addition, necrosis of the skin resulted in marked scarring. In human subjects, concentrations of about 5 mg/m^3 were objectionable, usually causing cough, an increase in respiratory rate, and impairment of ventilatory capacity. Workers exposed to concentrations of 12.6 to 35 mg/m^3 had a markedly higher incidence of erosion and discoloration of teeth than was noted in unexposed individuals. Splashed in the eye, the concentrated acid causes extremely severe damage, often leading to blindness, whereas dilute acid produces more transient effects from which recovery may be complete. Repeated exposure of workers to the mist causes chronic conjunctivitis, tracheobronchitis, stomatitis, and dermatitis, as well as dental erosion. While ingestion of the liquid is unlikely in ordinary industrial use, the highly corrosive nature of the substance may be expected to produce serious mucous membrane burns of the mouth and esophagus.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 98
2. Boiling point (760 mm Hg): 270 C (518 F)
3. Specific gravity (water = 1): 1.84
4. Vapor density (air = 1 at boiling point of sulfuric acid): 3.4
5. Melting point: 3 C (37 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): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of acid with organic materials (such as chlorates, carbides, fulminates, and picrates) may cause fires and explosions. Contact of acid with metals may form toxic sulfur dioxide fumes and flammable hydrogen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfuric acid fume, sulfur dioxide, and carbon monoxide) may be released when sulfuric acid decomposes.
4. Special precautions: Liquid sulfuric acid will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Sulfuric acid is not combustible by itself, but is highly reactive and capable of igniting finely divided combustible materials on contact. Fires involving small amounts of combustibles may be smothered with dry chemical. Water applied directly to sulfuric acid causes evolution of heat and splattering.

- **Warning properties**

The International Labour Office (ILO) reports that sulfuric acid, in liquid or vapor form, can cause eye irritation, but no quantitative information is given. The NIOSH criteria document for sulfuric acid states that Bushtueva exposed 10 human subjects to different concentrations of sulfuric acid aerosol. At a concentration of 1.1 to 2.4 mg/m^3, 40% of the subjects experienced 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 sulfuric acid on a cellulose membrane filter, followed by extraction with distilled water and isopropyl alcohol, treatment with perchloric acid, and titration with barium perchlorate. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sulfuric acid may be used. An analytical method for sulfuric 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 sulfuric acid or solutions containing more than 1% sulfuric acid 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 solutions containing 1% or less sulfuric acid by weight.

• Where there is any possibility of exposure of an employee's body to liquid sulfuric acid or solutions containingmore than 1% sulfuric acid 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 sulfuric acid should be removed immediately and not reworn until the sulfuric acid is removed from the clothing.

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

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid sulfuric acid or solutions containing sulfuric acid contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid sulfuric acid or solutions containimore than 1% sulfuric acid by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in manufacture of phosphoric acid and fertilizers	Process enclosure; local exhaust ventilation; personal protective equipment
Use in petroleum refining as an alkylation catalyst for production of high-octane gasoline, production of jet fuels, kerosene, lube and white oils, oil additives, and preparation of cracking catalysts	Process enclosure; local exhaust ventilation; personal protective equipment
Use during manufacture of pigments and dyes, and dyestuff intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of industrial and military explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of alcohols, phenols, and inorganic sulfates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in ore leaching and processing; use in metal cleaning and plating; manufacture of electrogalvanized wire; anodizing of metal; electroplating	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of detergents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in coke-oven gas refining; use in plastics industry for manufacture of rayon, cellophane, cellulose, acetate, caprolactam, and others; use in lead storage batteries as electrolyte	Process enclosure; local exhaust ventilation; personal protective equipment
Use in food processing in manufacture of brewing sugars for beer, manufacture of glucose, refining of mineral and vegetable oils	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Use for preparation of insecticides; use in manufacture of natural and synthetic rubber	Process enclosure; local exhaust ventilation; personal protective equipment
Use for gas drying to dry acid and corrosive gases; use in treatment of industrial water for pH control	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of textiles and leather for treatment of wool, pickling leather, as a dye assist, as a solvent for vat dyes, and in fabric finishing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a laboratory reagent as a solvent and for chemical analysis; use in chemical synthesis in preparation of acids, intermediates for medicinals, gas, esters, and fatty acids	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 sulfuric acid or solutions containing sulfuric 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 liquid sulfuric acid or solutions containing sulfuric acid get on the skin, immediately flush the contaminated skin with water. If liquid sulfuric acid or solutions containing sulfuric acid 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 sulfuric 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 liquid sulfuric acid or solutions containing sulfuric acid have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the sulfuric 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 sulfuric acid is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled or leaked material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Sulfuric acid should be absorbed in vermiculite, dry sand, earth, or a similar material. It may also be diluted and neutralized.

- Waste disposal method:

Sulfuric acid may be placed in sealed containers or absorbed in vermiculite, dry sand, earth, or a similar material and disposed of in a secured sanitary landfill. It may also be diluted and neutralized.

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RESPIRATORY PROTECTION FOR SULFURIC ACID

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
50 mg/m³ or less	A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter. A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Sulfur Monochloride

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: S_2Cl_2
- Synonyms: Sulfur chloride; sulfur subchloride
- Appearance and odor: Amber to red fuming, oily liquid with a pungent, nauseating, and irritating odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfur monochloride is 1 part of sulfur monochloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of sulfur monochloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfur monochloride 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: Vapors of sulfur monochloride may cause coughing, and tearing and burning of the eyes which may be delayed in onset. Inhalation of high concentrations of sulfur monochloride may cause severe difficulty in breathing and symptoms of chemical pneumonia. If splashed on the skin, sulfur monochloride liquid may cause irritation, and, if allowed to remain on the skin, a burn. If the liquid is splashed in the eyes, it may produce severe, immediate damage and scarring.

2. Long-term Exposure: Repeated exposure of the skin, eyes, or upper respiratory tract to sulfur monochloride may cause chronic 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 sulfur monochloride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfur monochloride 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: Sulfur monochloride is a respiratory irritant. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfur monochloride 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**

Sulfur monochloride is a severe irritant of the eyes, mucous membranes, and skin. On contact with water it decomposes to form hydrogen chloride and sulfur dioxide; since this occurs rapidly, it acts primarily as an upper respiratory irritant and does not ordinarily reach the lungs. Exposure of mice to 150 ppm for 1 minute is fatal. In humans, exposure to the vapor causes lacrimation and cough; exposure to high concentrations may cause pulmonary edema. Concentrations of 2 to 9 ppm are reported to be mildly irritating. Splashes of 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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liquid in the eyes will produce severe immediate damage which may result in permanent scarring. The liquid on the skin will produce irritation and burns if not removed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 135
2. Boiling point (760 mm Hg): 138 C (280 F)
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of sulfur monochloride): 4.66
5. Melting point: −76 C (−105 F)
6. Vapor pressure at 20 C (68 F): 6.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts violently, forming hydrochloric acid
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Temperatures above 300 C (572 F) cause decomposition to toxic chlorine gas and solid sulfur.
2. Incompatibilities: Contact with peroxides, oxides of phosphorus, and some organic matter may cause fires and explosions. Contact with water causes a violent reaction, forming hydrogen chloride gas (or hydrochloric acid), which may corrode metal containers and form flammable hydrogen gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, sulfur dioxide, hydrogen sulfide, and carbon monoxide) may be released in a fire involving sulfur monochloride.
4. Special precautions: Sulfur monochloride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 118.5 C (245 F) (closed cup)
2. Autoignition temperature: 234 C (453 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No information is available concerning the odor threshold of sulfur monochloride.
2. Eye Irritation Level: According to Grant, "even 2 to 9 ppm in air are said to be mildly irritating to the eyes."
3. Evaluation of Warning Properties: Since sulfur monochloride causes eye irritation within twice the permissible exposure limit, this substance 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**

At the time of publication of this guideline, no measurement method for sulfur monochloride 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 sulfur monochloride.
- Clothing contaminated with sulfur monochloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sulfur monochloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sulfur monochloride, the person performing the operation should be informed of sulfur monochloride's hazardous properties.
- Where there is any possibility of exposure of an employee's body to liquid sulfur monochloride, 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 sulfur monochloride should be removed immediately and not reworn until the sulfur monochloride 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 sulfur monochloride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid sulfur monochloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

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

Operation	Controls
Use for production of white vulcanized oils used for coating and impregnating textiles; use as natural and synthetic rubber extenders and modifying agents in erasers, and extruded rubber goods	Process enclosure; local exhaust ventilation; personal protective equipment
Use with unsaturated fatty acids in production of additives to extreme pressure lubricants and cutting oils	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a cross-linking catalyst in polymer technology; use in chemical synthesis for production of intermediates for dyes, pharmaceuticals, insecticides, and war gases	Process enclosure; local exhaust ventilation; personal protective equipment
Use for treatment of drying oils for production of varnishes, inks, paints, and cements; use for cold vulcanizing of thin rubber articles; use as a solvent for sulfur and sulfur compounds	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 sulfur monochloride or strong concentrations of sulfur monochloride 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 sulfur monochloride or strong concentrations of sulfur monochloride vapor get on the skin, immediately flush the contaminated skin with water. If liquid sulfur monochloride or strong concentrations of sulfur monochloride vapor penetrate 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 sulfur monochloride, 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 sulfur monochloride has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the sulfur monochloride. Do not induce vomiting. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

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

• If sulfur monochloride is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Spray on a thick layer of a (1:1) mixture of dry soda ash and slaked lime. Mix and spray on water slowly, then add large amounts of water. The neutralized solution can then be disposed in a secured sanitary landfill.

• Waste disposal method:

Sulfur monochloride may be disposed of by using (2) above.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Sulfur Monochloride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Manufacturing Chemists Association, Inc.: *Chemical Safety Data Sheet SD-77, Sulfur Monochloride*, Washington, D.C., 1960.
- 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* (4th ed.), Van Nostrand Reinhold, New York, 1975.

RESPIRATORY PROTECTION FOR SULFUR MONOCHLORIDE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
10 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) for hydrogen chloride and sulfur dioxide. A gas mask with a chin-style or a front- or back-mounted canister for hydrogen chloride and sulfur dioxide. 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 hydrogen chloride and sulfur dioxide. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Sulfur Pentafluoride

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: S_2F_{10}
- Synonyms: Disulfur decafluoride
- Appearance and odor: Colorless liquid or gas with an odor like sulfur dioxide.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfur pentafluoride is 0.025 part of sulfur pentafluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.25 milligram of sulfur pentafluoride per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfur pentafluoride can affect the body if it is inhaled. No data could be found in the literature which specifically reported possible effects of eye or skin contact with the liquid or the effects of ingestion.

- **Effects of overexposure**

1. Short-term Exposure: In animals, inhalation has been reported to cause severe breathing difficulties.

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 sulfur pentafluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfur pentafluoride 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: Sulfur pentafluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfur pentafluoride 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**

Sulfur pentafluoride vapor is a severe pulmonary irritant. Exposure of rats to 1 ppm for 16 to 18 hours was fatal; 0.5 ppm caused pulmonary edema and hemorrhage; 0.1 ppm caused irritation of the lungs; 0.01 ppm had no discernible effects. Nonfatal exposure of rats for 1 hour to 10 ppm caused pulmonary hemorrhage. In rabbits the LD50 for intravenous injection of a lecithin emulsion of sulfur pentafluoride was 5.8 mg/kg; at autopsy the chief lesion was massive pulmonary edema with frequent hemorrhage, apparently a result of widespread endothelial damage to the cardiovascular system.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 254
2. Boiling point (760 mm Hg): 29 C (84 F)
3. Specific gravity (water = 1): 2.08 (at 0 C)
4. Vapor density (air = 1 at boiling point of sulfur

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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pentafluoride): 8.75

5. Melting point: −55 C (−67 F)
6. Vapor pressure at 20 C (68 F): 561 mm Hg
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: Temperatures above 400 C (752 F) cause decomposition and development of pressure in containers.
2. Incompatibilities: None
3. Hazardous decomposition products: None
4. Special precautions: None

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: No quantitative information is available.
2. Eye Irritation Level: According to the International Labour Office (ILO), "no data are available on its effects on the upper respiratory tract and conjunctivae."
3. Evaluation of Warning Properties: Since no quantitative information available relating its warning properties to air concentrations, sulfur pentafluoride 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 sulfur pentafluoride 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 sulfur pentafluoride or liquids containing sulfur pentafluoride.

• Clothing contaminated with sulfur pentafluoride should be stored in such a manner that the sulfur pentafluoride is not dispersed until it can be discarded, or until provision is made for the removal of sulfur pentafluoride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sulfur pentafluoride, the person performing the operation should be informed of sulfur pentafluoride's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid sulfur pentafluoride, 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 sulfur pentafluoride should be removed immediately and not reworn until the sulfur pentafluoride 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 sulfur pentafluoride or liquids containing sulfur pentafluoride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid sulfur pentafluoride or liquids containing sulfur pentafluoride, an eye-wash fountain should be provided within the immediate work area for emergency use.

• Employees should immediately evacuate the area whenever sulfur pentafluoride is accidentally released into the workplace air.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation as a by-product during synthesis of sulfur hexafluoride (This compound is considered more toxic than phosgene and is not produced commercially).	Provisions should be made to exit vapors so that they are absorbed by activated alumina and soda lime

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 sulfur pentafluoride or liquids containing sulfur pentafluoride 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 sulfur pentafluoride or liquids containing sulfur pentafluoride get on the skin, immediately flush the contaminated skin with water. If liquid sulfur pentafluoride or liquids containing sulfur pentafluoride penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of sulfur pentafluoride, 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 sulfur pentafluoride or liquids containing sulfur pentafluoride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the sulfur pentafluoride. 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 sulfur pentafluoride is spilled or leaked, the following steps should be taken:

1. Ventilate area of leak.
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.
3. If liquid, allow liquid to evaporate.

ADDITIONAL INFORMATION

To find additional information on sulfur pentafluoride, look up sulfur pentafluoride 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

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

• Greenberg, L. A., and Lester, D.: "The Toxicity of Sulfur Pentafluoride," *A.M.A. Archives of Industrial Hygiene and Occupational Medicine,* 2:350-352, 1950.

• International Labour Office: *Encyclopedia of Occupational Health and Safety,* McGraw-Hill, New York, 1971.

• Saunders, J. P., et al.: "Some Physiological Effects of Disulfur Decafluoride (S_2F_{10}) after Intravenous Injection in Dogs," *A.M.A. Archives of Industrial Hygiene and Occupational Medicine,* 8:436-445, 1953.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

• Stauden, A. (exec. ed.): *Kirk-Othmer Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1972.

RESPIRATORY PROTECTION FOR SULFUR PENTAFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 0.025 ppm
Vapor Concentration	
0.25 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1 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 1 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 Sulfuryl 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: SO_2F_2
- Synonyms: None
- Appearance and odor: Colorless and odorless gas.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfuryl fluoride is 5 parts of sulfuryl fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 20 milligrams of sulfuryl fluoride per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfuryl fluoride can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

1. Short-term Exposure: Animal experiments have shown that inhalation of sulfuryl fluoride may cause shaking, convulsions, and severe breathing difficulties. Human exposure to a mixture of sulfuryl fluoride and an irritant gas caused nausea, vomiting, crampy abdominal pain, itching, reddening of the eyes, nose, and throat, and minor lung changes. These effects were of short duration.

2. Long-term Exposure: Animal experiments have shown that repeated exposure to sulfuryl fluoride may cause mottled teeth and kidney and lung injury.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfuryl fluoride.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfuryl 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 system and the central nervous system should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Sulfuryl fluoride gas is a respiratory irritant and a depressant of the central nervous system. Although there are few details, exposure of animals to an unspecified but high concentration caused signs of narcosis and, in some instances, tremor, convulsions, and pulmonary edema; repeated exposure caused lung and kidney injury. A worker who was exposed to an undetermined concentration of a mixture of sulfuryl fluoride and an undesignated irritant gas for 4 hours developed nausea, vomiting, abdominal pain, and pruritis; examination revealed conjunctivitis, rhinitis, pharyngitis, diffuse rhonchi, and paresthesia of the right leg, all of which rapidly subsided.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 102.1
2. Boiling point (760 mm Hg): −55.2 C (−67 F)
3. Specific gravity (water = 1): 1.36 (liquid)
4. Vapor density (air = 1 at boiling point of sulfuryl fluoride): 3.5
5. Melting point: −136.7 C (−213 F)
6. Vapor pressure at 20 C (68 F): Greater than 1

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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atmosphere

7. Solubility in water, g/100 g water at 20 C (68 F): 0.16

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: High temperatures may cause cylinders to burst.

2. Incompatibilities: None

3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and hydrogen fluoride) may be released when sulfuryl fluoride decomposes.

4. Special precautions: See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: Spector states that sulfuryl fluoride is odorless.

2. Eye Irritation Level: Baskin states that sulfuryl fluoride is severely irritating to the eyes. Other sources do not mention this severe eye irritation, however, and no quantitative information is available concerning the threshold of eye irritation. Gleason states that "chronic exposure . . . . to 100 ppm resulted in no adverse effects on rats, rabbits, guinea pigs, or monkeys."

3. Other Information: Baskin states that sulfuryl fluoride is severely irritating to the mucous membranes of the respiratory tract. No quantitative information is available concerning the threshold of this irritation, however.

4. Evaluation of Warning Properties: Since sulfuryl fluoride is odorless, and since no quantitative information is available relating its irritant effects to air concentrations, this substance is treated as a material with poor warning properties. Taxay states that sulfuryl fluoride has no 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 sulfuryl fluoride 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.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during use as an insecticidal fumigant for control of dry wood termites and other structural pests	Process enclosure; mix with alerting gas

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 sulfuryl fluoride gas 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.

• **Breathing**

If a person breathes in large amounts of sulfuryl 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. Under-

stand 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 sulfuryl 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 inplace, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty into a mixed solution of caustic soda and slaked lime.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Sulfuryl Fluoride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Baskin, A. D. (ed.): *Handling Guide for Potentially Hazardous Commodities*, Railway Systems and Management Association, Chicago, 1972.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- 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, Philadelphia, 1956-1959.
- Taxay, E. P.: "Vikane Inhalation," *Journal of Occupational Medicine*, 8:425-426, 1966.

RESPIRATORY PROTECTION FOR SULFURYL FLUORIDE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas 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.
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 sulfuryl fluoride. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for 2,4,5-T *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Cl_3C_6H_2OCH_2COOH$
- Synonyms: 2,4,5-Trichlorophenoxyacetic acid
- Appearance and odor: Colorless to tan odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2,4,5-T is 10 milligrams of 2,4,5-T per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2,4,5-T 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 2,4,5-T may cause abdominal pain, nausea, vomiting, diarrhea, and blood in the stool. It may also cause irritation of the skin. Common contaminants of commercial preparations of 2,4,5-T may cause acne and liver damage. Animal experiments have shown that these contaminants may produce damage in unborn rats.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2,4,5-T.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2,4,5-T at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and attention to gastrointestinal complaints 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**

2,4,5-T (2,4,5-trichlorophenoxyacetic acid) is of low toxicity. The oral LD50 for dogs is in the range of 100 mg/kg or higher; effects are limited to a slight or moderate stiffness in the hind legs with development of ataxia. Contaminants of commercial preparations of 2,4,5-T have been 2,3,7,8-tetrachlorodibenzo-p-dioxin, a potent animal teratogen, and 2,3,6,7-tetrachlorodibenzo-p-dioxin (TCDD), a potent acnegenic agent which is hepatotoxic in animals; they are present as unwanted side products of synthesis of 2,4,5-T. In a study of 73 workers in a 2,4,5-T manufacturing plant, 13 had moderate to severe acneform dermatitis (chloracne) and 22 had gastrointestinal complaints such as nausea, vomiting, diarrhea, abdominal pain, or blood in the stool; no significant liver dysfunction was found; although no air sample results were reported, the chloracne was thought to be a result of exposure to TCDD. 2,4,5-T dust is a slight irritant of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 255.5
2. Boiling point (760 mm Hg): Decomposes above melting point
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of 2,4,5-T): Not applicable
5. Melting point: 158 C (316 F) (decomposition)

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): 0.03

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Temperatures above 158 C (316 F) may cause sealed metal containers to burst.

2. Incompatibilities: None.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when 2,4,5-T decomposes.

4. Special precautions: None.

• **Flammability**

1. Not combustible

• **Warning properties**

2,4,5-T 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 2,4,5-T 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 2,4,5-T is handled, processed, or stored.

• Employees who handle 2,4,5-T should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2,4,5-T may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of herbicides and plant hormones	Process enclosure; local exhaust ventilation; personal protective equipment
Application as herbicide, defoliant, and plant hormone	Personal protective equipment
Manufacture of 2,4,5-T	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 2,4,5-T 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 2,4,5-T or liquids containing 2,4,5-T get on the skin, wash the contaminated skin using soap or mild detergent and water. If 2,4,5-T or liquids containing 2,4,5-T soak through the clothing, remove the clothing 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 2,4,5-T, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When 2,4,5-T or liquids containing 2,4,5-T 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 2,4,5-T 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 2,4,5-T should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

2,4,5-T may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "2,4,5-T (2,4,5-Trichlorophenoxacetic Acid)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 1977.

RESPIRATORY PROTECTION FOR 2,4,5-T

Condition	Minimum Respiratory Protection* Required Above 10 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any dust and mist respirator, except single-use.
100 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.
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.
5000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Talc (Non-Asbestos Form)

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 specific formula
- Synonyms: Hydrous magnesium silicate; steatite talc; non-fibrous talc; non-asbestiform talc
- Appearance and odor: Odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for talc is 20 million particles of talc per cubic foot of air (mppcf) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for talc (non-asbestos form) from 20 mppcf to 15 mppcf or 2 mg/m³ respirable dust.

•Method

At the time of publication of this guideline, no measurement method for talc had been published by NIOSH.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Talc can affect the body if it is inhaled or if it comes in contact with the eyes.

- **Effects of overexposure**

Repeated inhalation of non-asbestos form of talc dust might cause scarring of the lungs with shortness of breath, chronic cough, and heart failure. The non-asbestos form of talc may cause irritation of the eyes in the same manner as nuisance dusts.

- **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 talc.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to talc 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 cardiovascular system should be stressed.

—14" x 17" chest roentgenogram: The non-asbestos form of talc may have the potential to cause pulmonary fibrosis and cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Talc 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**

The non-asbestos form of talc, also termed nonfibrous, has been reported to cause talcosis although this is controversial. It has not been proven to cause the effects produced by exposure to fibrous talc: fibrotic pneumoconiosis and an increased incidence of cancer of the lungs and pleura. In a study of 20 workers exposed for 10 to 36 years to talc described as "pure," at levels ranging from 15 to 35 mppcf, no evidence of pneumoconiosis was found. In another study which compared the pulmonary function of workers exposed to either fibrous or nonfibrous talc, it was concluded that while the fibrous form was the more pathogenic type, both talcs produced pulmonary fibrosis; no data were presented to document the types of talc involved. An epidemiologic study of 260 workers with 15 or more

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

years of exposure to commercial talc dust containing pure talc, plus tremolite, anthophyllite, carbonate dusts, and a small amount of free silica revealed a fourfold greater than expected proportional mortality from cancer of the lungs and pleura; in addition, a major cause of death was cor pulmonale, a result of the pneumoconiosis; the effects were likely due to the asbestos-form contaminants. The role of nonfibrous talc in these disease states could not be assessed.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 295
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 2.5 – 2.8
  4. Vapor density (air = 1 at boiling point of talc): Not applicable
  5. Melting point: 900 – 1000 C (1652 – 1832 F) (loses water)
  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: None
  3. Hazardous decomposition products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Talc is not reported to be a significant eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of talc in an impinger, followed by dust counting utilizing an optical microscope. A detailed analytical method for talc 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 R" (order number PB 262 403).

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 talc may occur and control methods which may be effective in each case:

Operation	Controls
Use in cosmetic industry as face powder, body or dusting powder, soap, and toilet preparations; in pharmaceutical industry in tablets, pills, salves, and lotions	General dilution ventilation; dust collecting system; wet grinding; personal protective equipment
Liberation during mining and processing by crushing, drying, milling, and upgrading by flotation	General dilution ventilation; dust collecting system; wet grinding; personal protective equipment
Use as a filler and selective absorbent in paper industry; use in ceramics industry in high quality electronic products as insulation; use as a selective absorbent in rubber and plastics reinforcing; use in cleaning up oil spills	General dilution 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 the non-asbestos form of talc 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.

SPILL AND DISPOSAL PROCEDURES

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

• If talc 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.

• Waste disposal method:

Talc may be disposed of in a secured sanitary landfill.

REFERENCES

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• Spiegel, R. M.: "Medical Aspects of Talc" in A. Goodwin (ed.), *Proceedings of the Symposium on Talc,* Washington, D.C., May 8, 1973, Bureau of Mines Report No.8639, U.S. Government Printing Office, Washington, D.C., pp.97-102, 1973.

RESPIRATORY PROTECTION FOR TALC (NON-ASBESTOS FORM)

Condition	Minimum Respiratory Protection* Required Above 20 mppcf
Particulate Concentration	
100 mppcf or less	Any dust and mist respirator.
200 mppcf 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.
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 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 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 Tantalum Metal and Oxide Dusts

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

Metallic tantalum

- Formula: Ta
- Synonyms: None
- Appearance and odor: Gray-black, odorless solid.

Tantalum pentoxide

- Formula: Ta_2O_5
- Synonyms: None
- Appearance: Colorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tantalum can affect the body if it is inhaled.

- **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 tantalum.

- **Recommended medical surveillance**

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

- **Summary of toxicology**

Tantalum dust has a low order of toxicity but has produced transient inflammatory lesions in the lungs of animals. Intratracheal administration of tantalum oxide to guinea pigs produced transient bronchitis, interstitial pneumonitis, and hyperemia. There were some slight residual sequelae in the form of focal hypertrophic emphysema and organizing pneumonitis around metallic deposits; there was slight epithelial hyperplasia in the bronchi and bronchioles.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Metallic tantalum**
  1. Molecular weight: 180.9
  2. Boiling point (760 mm Hg): 5425 C (9997 F)
  3. Specific gravity (water = 1): 16.6
  4. Vapor density (air = 1 at boiling point of tantalum): Not applicable
  5. Melting point: 2980 C (5396 F)
  6. Vapor pressure at 20 C (68 F): 0 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Physical data—Tantalum pentoxide**
  1. Molecular weight: 441.89
  2. Boiling point (760 mm Hg): Not applicable
  3. Specific gravity (water = 1): 8.2
  4. Vapor density (air = 1 at boiling point of tantalum pentoxide): Not applicable
  5. Melting point: 1800 C (3272 F)
  6. Vapor pressure at 20 C (68 F): Not applicable
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity—Metallic tantalum**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact of tantalum (metallic dust) with strong oxidizers may cause fires and explo-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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National Institute for Occupational Safety and Health

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Occupational Safety and Health Administration

sions.

3. Hazardous decomposition products: None

4. Special precautions: None

• **Flammability-Metallic tantalum**

1. Flash point: Not applicable

2. Minimum ignition temperature: 300 C (572 F) (layer); 630 C (1166 F) (cloud)

3. Minimum explosion dust concentration: Less than 0.2 g/l

4. Extinguishant: Dry sand, dry dolomite, and dry graphite

• **Warning properties**

Tantalum 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 tantalum 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 tantalum metal and oxide dusts may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during refining ores, manufacture of tantalum compounds, metal, and alloys	General dilution ventilation; local exhaust ventilation
Use in fabrication for manufacture of electronic equipment such as electrolytic capacitors used in solid-state circuitry for computers, instrumentation, and consumer items, and high-voltage surge arrestors	General dilution ventilation; local exhaust ventilation
Use in fabrication of metals for manufacture of chemical and metallurgical processing equipment and heat exchanger	General dilution ventilation; local exhaust ventilation
Use in fabrication of refractory non-ferrous alloys for nuclear and aerospace applications; use in manufacture of tantalum carbide for working machinery; use in manufacture of surgical metals, mesh, and clips; use in manufacture of special optical glass; and use in manufacture and repair of glass-lined equipment	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.

• **Breathing**

If a person breathes in large amounts of metallic tantalum dust or tantalum oxide 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—Metallic tantalum and tantalum pentoxide

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

• If potentially hazardous amounts of metallic tantalum or tantalum pentoxide are spilled or released, the following steps should be taken:

1. Remove all ignition sources in the case of a spill or release of metallic tantalum dust.
2. Ventilate area of spill or release.
3. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill.

• Waste disposal method:

Tantalum and tantalum pentoxide may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR TANTALUM

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Dust or Mist Concentration	
25 mg/m³ or less	Any dust and mist respirator.
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 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 TEDP

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: $(C_2H_5)_4P_2S_2O_5$
- Synonyms: Tetraethyl pyrophosphorodithionate; sulfotepp; tetraethyl dithionopyrophosphate; tetraethyl dithiopyrophosphate
- Appearance and odor: Yellow liquid wtih a garlic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

TEDP 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 TEDP, 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 TEDP, loss of appetite, nausea, vomiting, abdominal cramps, and diarrhea may appear within 2 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 heartbeat, convulsions, and coma may occur.

2. Long-term Exposure: Repeated exposure to levels of TEDP 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 TEDP.

- **Recommended medical surveillance**

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

—Cholinesterase determination: TEDP 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 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**

TEDP (tetraethyl dithionopyrophosphate) is an anticholinesterase agent; absorption may occur from inhalation of the mist, 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 at synapses 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, 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 one week; increased susceptibility to the effects of anticholinesterase agents persists for one to several days after exposure. Daily exposure to concentrations which are insufficient to produce symptoms following a single exposure may result in the onset of symptoms. Continued daily exposure may be followed by increasingly severe effects.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 322.2
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.19
4. Vapor density (air = 1 at boiling point of TEDP): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0025
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 may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, phosphoric acid mist, and carbon monoxide) may be released when TEDP decomposes.
4. Special precautions: TEDP will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

1. Odor Threshold: No quantitative information available concerning the odor threshold of TEDP.
2. Eye Irritation Level: TEDP 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 TEDP, 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 TEDP 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 TEDP.

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

• Where there is any possibility of exposure of an employee's body to TEDP, 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 TEDP should be removed immediately and not reworn until the TEDP is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of TEDP contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to TEDP, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

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

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

Operation	Controls
Formulation of insecticides	Process enclosure; local exhaust ventilation; personal protective equipment
Application of insecticide by aerosol or fumigation on flowering plants in commercial greenhouses	Personal protective equipment
Manufacture of TEDP	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 TEDP or formulations containing TEDP 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 TEDP or formulations containing TEDP get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If TEDP or formulations containing TEDP 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 TEDP, 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 TEDP or formulations containing TEDP 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 TEDP is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

TEDP 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.

REFERENCES

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RESPIRATORY PROTECTION FOR TEDP

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m³
Particulate or Vapor Concentration	
2 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
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.
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 TEDP; 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 Tellurium and Compounds (as Tellurium)

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 tellurium and compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Tellurium

- Formula: Te
- Synonyms: Tellurium, metallic
- Appearance and odor: Odorless, grayish-colored solid with a metallic luster.

Hydrogen telluride

- Formula: H_2Te
- Synonyms: Tellurium hydride
- Appearance and odor: Colorless gas with a characteristic odor like arsenic.

Potassium tellurite

- Formula: K_2TeO_3
- Synonyms: None
- Appearance and odor: White, odorless solid.

Sodium tellurate

- Formula: $Na_2H_4TeO_6$
- Synonyms: Sodium tellurate dihydrate
- Appearance and odor: White, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tellurium and compounds (as tellurium) is 0.1 milligram of tellurium and compounds (as tellurium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tellurium and compounds can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed. They may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Tellurium, hydrogen telluride, potassium tellurite, or sodium tellurate causes garlic odor of the breath and sweat, dryness of the mouth, metallic taste, sleepiness, loss of appetite, and nausea. Tellurium dioxide exposure may cause a temporary loss of sweat function.

2. Long-term Exposure: Tellurium hydride is highly toxic. It has produced irritation of the lungs and destruction of red blood cells in animals.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tellurium and compounds.

- **Recommended medical surveillance**

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

—Skin disease: Tellurium 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.

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

—Neurologic disorders: By analogy to effects observed in experimental animals, tellurium may adversely affect the nervous system in man.

—Blood disease: Hydrogen telluride is reported to cause hemolysis in animals. Persons with pre-existing blood disorders may be at increased risk from exposure.

—Chronic respiratory disease: Hydrogen telluride and other gaseous compounds of tellurium are reported to cause pulmonary effects. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of certain compounds of tellurium might cause exacerbation of symptoms.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination. The concentration of tellurium in the urine may be informative when exposures are high. Garlic odor of the breath is a sensitive sign of tellurium exposure.

• **Summary of toxicology**

Fume or dust of tellurium and its compounds causes garlic odor of the breath and malaise in humans. In animals, acute tellurium intoxication results in restlessness, tremor, diminished reflexes, paralysis, convulsions, somnolence, coma, and death. Tellurium compounds are more toxic than the metal. Administration to pregnant rats of 500 to 3000 ppm tellurium in the diet resulted in high incidence of hydrocephalic offspring. Weaning rats fed elemental tellurium at a level of 1% (10,000 ppm) in the diet developed a neuropathy characterized by segmental demyelination; remyelination and functional recovery occurred despite continued administration of tellurium. Iron foundry workers exposed to concentrations between 0.01 to 0.1 mg/m³ complained of garlic odor of the breath and sweat, dryness of the mouth and metallic taste, somnolence, anorexia, and occasional nausea; urinary concentrations ranged from zero to 0.06 mg/l; somnolence and metallic taste in the mouth did not appear with regularity until the level of tellurium in the urine was at least 0.01 mg/l. Skin lesions in the form of scaly, itching patches and loss of sweat function occurred in workers exposed to tellurium dioxide in an electrolytic lead refinery. Hydrogen telluride is highly toxic and has caused pulmonary irritation and hemolysis of red blood cells in animals; this gas is very unstable, however, and its occurrence as an actual industrial hazard is unlikely.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Tellurium**

1. Molecular weight: 127.6
2. Boiling point (760 mm Hg): 1390 C (2534 F)
3. Specific gravity (water = 1): 6.24
4. Vapor density (air = 1 at boiling point of tellurium): Not applicable
5. Melting point: 450 C (842 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—Hydrogen telluride**

1. Molecular weight: 129.6
2. Boiling point (760 mm Hg): −2 C (28 F)
3. Specific gravity (water = 1): 2.6 (liquid)
4. Vapor density (air = 1 at boiling point of hydrogen telluride): 4.5
5. Melting point: −50 C (−58 F)
6. Vapor pressure at 20 C (68 F): 1600 mm Hg approximately
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Potassium tellurite**

1. Molecular weight: 253.8
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of potassium tellurite): Not applicable
5. Melting point: 450 C (842 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): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium tellurate**

1. Molecular weight: 273.6
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of sodium tellurate): Not applicable
5. Melting point: 170 C (338 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): 0.8
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None. (Hydrogen telluride is unstable, but is rarely worked with as such).
2. Incompatibilities: Contact of tellurium metal or hydrogen telluride 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: a) Tellurium: 340 C (644 F) (layer); 550 C (1022 F) (cloud); b) Hydrogen telluride: Data not available; c) Potassium tellurite and d) sodium tellurate: Not applicable
3. Flammable limits in air, % by volume: Tellurium, potassium tellurite, and sodium tellurate: Not applicable; Hydrogen telluride: Data not available
4. Extinguishant: Tellurium: Water; Hydrogen telluride: Rarely handled as such; Potassium tellurite and

sodium tellurate: Not applicable

• **Warning properties**

Tellurium 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 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 tellurium and 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).

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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 frozen from contact with hydrogen telluride or from contact with vessels containing hydrogen telluride.

• 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 potassium tellurite, sodium tellurate, or liquids containing these compounds.

• If employees' clothing may have become contaminated with potassium tellurite, sodium tellurate, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with potassium tellurite or sodium tellurate 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.

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

• Non-impervious clothing which becomes contaminated with potassium tellurite should be removed promptly and not reworn until the potassium tellurite is removed from the clothing.

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

SANITATION

• Skin that becomes contaminated with potassium tellurite should be promptly washed or showered to remove any contaminant.

• Eating and smoking should not be permitted in areas where potassium tellurite, sodium tellurate, or liquids containing these compounds are handled, processed, or stored.

• Employees who handle potassium tellurite, sodium tellurate, or liquids containing these 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 tellurium and compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during recovery, purification, and packaging	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during manufacture of alloys with copper, steel, lead, tin, silver, magnesium, nickel, and phosphorus; during use in manufacture of cast iron; liberation during refining of various minerals	Process enclosure or local exhaust ventilation; personal protective equipment
Liberation during use in manufacture of natural and synthetic rubber and plastics	Process enclosure or local exhaust ventilation; personal protective equipment
Use in manufacture of tellurium compounds used as insecticides, germicides, fungicides, and photographic print toners	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use in ceramic colorants and glass manufacture; during manufacture of thermoelectric devices for cooling boxes, solar energy converters, and small control apparatus; during manufacture of electronic devices such as batteries, solar cells, and semiconductors, and during manufacture of tellurium compounds	Process enclosure or local exhaust ventilation; personal protective equipment
Liberation during refining of various minerals; during use as a catalyst for acrylic monomer production	Process enclosure or local exhaust ventilation; personal protective equipment
Use in manufacture of tellurium compounds used as insecticides, germicides, fungicides, and photographic print toners	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 tellurium and 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 tellurium and compounds get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tellurium and compounds penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention promptly.

- **Breathing**

If a person breathes in large amounts of tellurium and 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 tellurium and 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, 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 tellurium and compounds are spilled, the following steps should be taken:

1. Ventilate area of spill or leak.
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 tellurium and compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.
3. For hydrogen telluride, stop flow of gas.

- Waste disposal method:

Tellurium and compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR TELLURIUM AND COMPOUNDS (AS TELLURIUM)

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1 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.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
50 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any 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 Tellurium Hexafluoride

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: TeF_6
- Synonyms: None
- Appearance and odor: Colorless gas with a repulsive odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tellurium hexafluoride is 0.02 part of tellurium hexafluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.2 milligram of tellurium hexafluoride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tellurium hexafluoride can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Tellurium hexafluoride may cause a garlic odor to the breath, headaches, and difficulty in breathing. Tellurium exposure experience with animals indicates that delayed severe breathing difficulties might 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 tellurium hexafluoride.

- **Recommended medical surveillance**

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

—Chronic respiratory disease: Tellurium hexafluoride causes respiratory irritation. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of tellurium hexafluoride 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**

Tellurium hexafluoride gas is a severe respiratory irritant. Animals exposed to 1 ppm for 4 hours developed pulmonary edema; 5 ppm for 4 hours was fatal. Human experience has indicated that exposure to tellurium hexafluoride causes headache and dyspnea. No systemic effects have been reported from industrial exposure, but relatively few studies are available.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 241.6
2. Boiling point (760 mm Hg): −38.4 C (−38 F) (sublimes)
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of tellurium hexafluoride): 8.3
5. Melting point: −37.8 C (−36 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): Reacts slowly
8. Evaporation rate (butyl acetate = 1): Not perti-

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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- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride) may be released when tellurium hexafluoride decomposes.
4. Special precautions: See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of tellurium hexafluoride. The *Documentation of TLV's*, however, notes that this gas has an unpleasant odor.
2. Eye Irritation Level: Tellurium hexafluoride 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 compound 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 tellurium hexafluoride using an adsorption tube, followed by desorption with sodium hydroxide and atomic absorption spectrophotometric analysis. An analytical method for tellurium hexafluoride 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 tellurium hexafluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use in scientific studies on physical and chemical properties such as magnetic spin, force constants spectra, electron diffraction, crystal structure, and corrosive action	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.

- **Breathing**

If a person breathes in large amounts of tellurium hexafluoride, 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 tellurium hexafluoride 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

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

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RESPIRATORY PROTECTION FOR TELLURIUM HEXAFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 0.02 ppm
Gas Concentration	
0.2 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1 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 1 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 tellurium hexafluoride. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for TEPP

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: $(C_2H_5)_4P_2O_7$
- Synonyms: Tetraethyl pyrophosphate, commercial 40%; ethyl pyrophosphate; bladan; nifost; vapotone; tetron; killax; mortopal
- Appearance and odor: Colorless to amber liquid with a faint fruity odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for TEPP is 0.05 milligram of TEPP per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

TEPP can affect the body if it is inhaled or 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 TEPP, 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 TEPP, loss of appetite, nausea, vomiting, abdominal cramps, and diarrhea may appear within 2 hours. After skin absorption, sweating and twitching in the area of absorption may occur usually within 15 minutes to 4 hours. With severe intoxiciation 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 TEPP 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 TEPP.

- **Recommended medical surveillance**

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

—Cholinesterase determination: TEPP 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 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 or symptoms of toxicity occur.

• **Summary of toxicology**

TEPP (tetraethyl pyrophosphate) is an anticholinesterase agent; absorption may occur from inhalation of the mist, by skin absorption, or by 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 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 occurs promptly and almost always within 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 one week; increased susceptibility to the effects of anticholinesterase agents persists for one to several days 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. Mild intoxication was reported in 15 people exposed to a dust of 1% TEPP under unusual conditions of static air; the predominant symptom was shortness of breath which occurred after breathing the dust-laden air for 30 minutes; symptoms rapidly abated after exposure was terminated.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 290.2
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of TEPP): Not applicable
5. Melting point: Gradually sets to glass below 0 C (32 F)
6. Vapor pressure at 140 C (284 F): 1 mm
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Temperatures above 150 C (300 F) cause decomposition with formation of flammable ethylene gas.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid mist and carbon monoxide) may be released when TEPP decomposes.
4. Special precautions: TEPP 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 TEPP.
2. Eye Irritation Level: TEPP is not known to produce a local, irritant effect upon the eye. According to Grant, however, when absorbed by the eye, TEPP can cause visual disturbances.
3. Evaluation of Warning Properties: No quantitative information is available relating warning properties to air concentrations of TEPP. TEPP, therefore, 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 TEPP 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 TEPP.
- Clothing contaminated with TEPP should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of TEPP from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the TEPP, the person performing the operation should be informed of TEPP's hazardous properties.
- Where there is any possibility of exposure of an employee's body to TEPP, 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 TEPP should be removed immediately and not reworn until the TEPP is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of TEPP contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to TEPP, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with TEPP should be immediately washed or showered to remove any TEPP.
- Eating and smoking should not be permitted in areas where TEPP is handled, processed, or stored.
- Employees who handle TEPP 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 TEPP may occur and control methods which may be effective in each case:

Operation	Controls
Application as a contact insecticide on agricultural and ornamental crops, including use in greenhouses	Personal protective equipment
Formulation of insecticides	General dilution ventilation; personal protective equipment
Manufacture of TEPP	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 TEPP or formulations containing TEPP 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 TEPP or formulations containing TEPP get on the skin, immediately wash the contaminated skin with water. If TEPP or formulations containing TEPP penetrate through the clothing, remove the clothing immediately and wash the skin with water. Get medical attention immediately.

- **Breathing**

If a person breathes in large amounts of TEPP, 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 TEPP or formulations containing TEPP 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 TEPP 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:

TEPP 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 TEPP

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m³
Particulate or Vapor Concentration	
0.5 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2.5 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 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 TEPP; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 10 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Terphenyls

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: $C_{18}H_{14}$
- Synonyms: ortho-Terphenyl; meta-terphenyl; para-terphenyl; mixed terphenyls; diphenylbenzenes; triphenyls
- Appearance: Colorless or light yellow solids.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for terphenyls is a ceiling of 1 part of terphenyls per million parts of air (ppm). This may also be expressed as 9 milligrams of terphenyls per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for terphenyls a Threshold Limit Value of 0.5 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Terphenyls can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

Exposure to terphenyls may cause eye, skin, and respiratory 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 terphenyls.

- **Recommended medical surveillance**

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

—Skin disease: The hot vapors of the terphenyls have a primary irritant effect on the skin. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: Persons with acute or chronic respiratory diseases may be more susceptible to the effects of terphenyls, since transient changes in the mitochondria of alveolar cells have been demonstrated in the lungs of animals following such exposure.

—Liver disease: Persons with liver disease may be more susceptible to the effects of inhalation of terphenyls, since transient changes in hepatic cells have been demonstrated in the liver of animals following such exposure.

—Kidney disease: Although terphenyls are not recognized as renal toxins, the importance of this organ in the excretion of metabolites formed from absorbed terphenyls 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**

Experimental animals show conjunctival irritation from direct contact with terphenyls. Clinical studies of an exposed group of employees showed no ill effects from prolonged exposure to concentrations ranging from 0.1 to 0.9 mg/m³. Animals exposed to concentrations of three to five times these levels had slight cellular changes in the lungs and liver, as demonstrated by electron microscopy. Absorbed terphenyls are slowly metabolized and excreted in the urine as phenolic compounds and as glucuronides.

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: 230

2. Boiling point (760 mm Hg): 333 to 381 C (630 to 718 F)

3. Specific gravity (water = 1): 1.1 to 1.2

4. Vapor density (air = 1 at boiling point of terphenyls): Not applicable

5. Melting point: 56 to 213 C (133 to 415 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: None

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

4. Special precautions: None

• **Flammability**

1. Flash point: 163 to 207 C (325 to 405 F) (open cup)

2. Autoignition temperature: Data not available

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

4. Extinguishant: Carbon dioxide or dry chemical

• **Warning properties**

The *Documentation of TLV's* states that "the available toxicologic data indicate that terphenyls may produce eye, skin, and respiratory irritation; they may also cause sensitization, but this has not been shown in man. Workers exposed to dust and vapor experienced marked irritation at concentrations in air above 10 mg/m^3. On this basis, a threshold limit value of 1ppm (about 9.4 mg/m^3) as a ceiling value is recommended to prevent irritation of the eye and respiratory tract."

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of terphenyls. 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 terphenyls on a filter, followed by leaching with carbon disulfide, and gas chromatographic analysis. An analytical method for terphenyls 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 terphenyls.

• 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 terphenyls or liquids containing terphenyls.

• If employees' clothing may have become contaminated with solid terphenyls, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where there is any possibility of exposure of an employee's body to molten terphenyls, 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 terphenyls should be removed promptly and not reworn until the terphenyls are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of molten terphenyls contacting the eyes.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid

terphenyls or solutions containing terphenyls may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to molten terphenyls, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

• Employees who handle solid terphenyls or solutions containing terphenyls 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 terphenyls may occur and control methods which may be effective in each case:

Operation	Controls
Use during formulation of waxes, polishes, and resin body paints	Local exhaust ventilation; personal protective equipment
Liberation during application of resin body paints, solvents, waxes, and polishes	Personal protective equipment
Liberation during maintenance operations or following leaks in heat-transfer systems; during release of high-temperature lubricants; during distillation and other processing operations	Personal protective equipment
Liberation during manufacture of plastic scintillators; during process of flaking or crushing to produce solid terphenyls following distillation	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 terphenyls 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 these chemicals.

• **Skin Exposure**

If terphenyls dust or solutions containing terphenyls get on the skin, promptly wash or shower to remove any terphenyls from the skin. If molten terphenyls get on the skin, immediately wash or shower the contaminated skin to remove any terphenyls from the skin. If molten terphenyls soak 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 terphenyls, 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 terphenyls have 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 terphenyls are 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, 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:

Terphenyls may be disposed of:

1. By making packages of terphenyls in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving terphenyls in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Terphenyls," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd

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• Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.

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RESPIRATORY PROTECTION FOR TERPHENYLS

Condition	Minimum Respiratory Protection* Required Above 9 mg/m³
Particulate Concentration	
450 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.
3500 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 3500 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 Terphenyls

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: $C_{18}H_{14}$
- Synonyms: ortho-Terphenyl; meta-terphenyl; para-terphenyl; mixed terphenyls; diphenylbenzenes; triphenyls
- Appearance: Colorless or light yellow solids.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for terphenyls is a ceiling of 1 part of terphenyls per million parts of air (ppm). This may also be expressed as 9 milligrams of terphenyls per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has recommended for terphenyls a Threshold Limit Value of 0.5 ppm as a ceiling value.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Terphenyls can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

Exposure to terphenyls may cause eye, skin, and respiratory 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 terphenyls.

- **Recommended medical surveillance**

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

—Skin disease: The hot vapors of the terphenyls have a primary irritant effect on the skin. Persons with preexisting skin disorders may be more susceptible to the effects of this agent.

—Chronic respiratory disease: Persons with acute or chronic respiratory diseases may be more susceptible to the effects of terphenyls, since transient changes in the mitochondria of alveolar cells have been demonstrated in the lungs of animals following such exposure.

—Liver disease: Persons with liver disease may be more susceptible to the effects of inhalation of terphenyls, since transient changes in hepatic cells have been demonstrated in the liver of animals following such exposure.

—Kidney disease: Although terphenyls are not recognized as renal toxins, the importance of this organ in the excretion of metabolites formed from absorbed terphenyls 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**

Experimental animals show conjunctival irritation from direct contact with terphenyls. Clinical studies of an exposed group of employees showed no ill effects from prolonged exposure to concentrations ranging from 0.1 to 0.9 mg/m³. Animals exposed to concentrations of three to five times these levels had slight cellular changes in the lungs and liver, as demonstrated by electron microscopy. Absorbed terphenyls are slowly metabolized and excreted in the urine as phenolic compounds and as glucuronides.

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.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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

1. Molecular weight: 230

2. Boiling point (760 mm Hg): 333 to 381 C (630 to 718 F)

3. Specific gravity (water = 1): 1.1 to 1.2

4. Vapor density (air = 1 at boiling point of terphenyls): Not applicable

5. Melting point: 56 to 213 C (133 to 415 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: None

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

4. Special precautions: None

• **Flammability**

1. Flash point: 163 to 207 C (325 to 405 F) (open cup)

2. Autoignition temperature: Data not available

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

4. Extinguishant: Carbon dioxide or dry chemical

• **Warning properties**

The *Documentation of TLV's* states that "the available toxicologic data indicate that terphenyls may produce eye, skin, and respiratory irritation; they may also cause sensitization, but this has not been shown in man. Workers exposed to dust and vapor experienced marked irritation at concentrations in air above 10 mg/m^3. On this basis, a threshold limit value of 1ppm (about 9.4 mg/m^3) as a ceiling value is recommended to prevent irritation of the eye and respiratory tract."

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of terphenyls. 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 terphenyls on a filter, followed by leaching with carbon disulfide, and gas chromatographic analysis. An analytical method for terphenyls 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 terphenyls.

• 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 terphenyls or liquids containing terphenyls.

• If employees' clothing may have become contaminated with solid terphenyls, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where there is any possibility of exposure of an employee's body to molten terphenyls, 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 terphenyls should be removed promptly and not reworn until the terphenyls are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of molten terphenyls contacting the eyes.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid

terphenyls or solutions containing terphenyls may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to molten terphenyls, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

• Employees who handle solid terphenyls or solutions containing terphenyls 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 terphenyls may occur and control methods which may be effective in each case:

Operation	Controls
Use during formulation of waxes, polishes, and resin body paints	Local exhaust ventilation; personal protective equipment
Liberation during application of resin body paints, solvents, waxes, and polishes	Personal protective equipment
Liberation during maintenance operations or following leaks in heat-transfer systems; during release of high-temperature lubricants; during distillation and other processing operations	Personal protective equipment
Liberation during manufacture of plastic scintillators; during process of flaking or crushing to produce solid terphenyls following distillation	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 terphenyls 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 these chemicals.

• **Skin Exposure**

If terphenyls dust or solutions containing terphenyls get on the skin, promptly wash or shower to remove any terphenyls from the skin. If molten terphenyls get on the skin, immediately wash or shower the contaminated skin to remove any terphenyls from the skin. If molten terphenyls soak 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 terphenyls, 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 terphenyls have 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 terphenyls are 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, 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:

Terphenyls may be disposed of:

1. By making packages of terphenyls in paper or other flammable material and burning in a suitable combustion chamber.
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Terphenyls can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

- **Effects of overexposure**

Exposure to terphenyls may cause eye, skin, and respiratory 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 terphenyls.

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5. Melting point: 56 to 213 C (133 to 415 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: None

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

4. Special precautions: None

• **Flammability**

1. Flash point: 163 to 207 C (325 to 405 F) (open cup)

2. Autoignition temperature: Data not available

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If terphenyls have been swallowed, do not induce vomiting. Get medical attention immediately.

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• Waste disposal methods:

Terphenyls may be disposed of:

1. By making packages of terphenyls in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving terphenyls in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Terphenyls," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd

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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 TERPHENYLS

Condition	Minimum Respiratory Protection* Required Above 9 mg/m³
Particulate Concentration	
450 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.
3500 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 3500 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 1,1,1,2-Tetrachloro-2,2-Difluoroethane

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_3-$CClF_2$
- Synonyms: Halocarbon 112a; refrigerant 112a; 2,2-difluoro-1,1,1,2-tetrachloroethane
- Appearance and odor: Colorless liquid or solid with a slight ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,1,2-tetrachloro-2,2-difluoroethane is 500 parts of 1,1,1,2-tetrachloro-2,2-difluoroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4170 milligrams of 1,1,1,2-tetrachloro-2,2-difluoroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,1,2-Tetrachloro-2,2-difluoroethane 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: 1,1,1,2-Tetrachloro-2,2-difluoroethane might cause irritation of the skin and eyes. It might also cause drowsiness and difficulty in breathing.

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 1,1,1,2-tetrachloro-2,2-difluoroethane.

- **Recommended medical surveillance**

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

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

1,1,1,2-Tetrachloro-2,2-difluoroethane vapor is a narcotic. Rats exposed to 10,000 ppm for 1-½ to 2 hours showed signs of intoxication, and concentrations of 20,000 to 30,000 ppm were fatal. Rats succumbing to 15,000 ppm for 4 hours evidenced pulmonary congestion and edema with some hemorrhage. Application in alcohol to the skin of rabbits produced severe irritation, while no irritation was reported when applied with dimethylphthalate. There are no reports of systemic effects in workers from industrial exposure.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 203.8
2. Boiling point (760 mm Hg): 92 C (197 F)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of 1,1,1,2-tetrachloro-2,2-difluoroethane): 7
5. Melting point: 40.6 C (105 F)
6. Vapor pressure at 20 C (68 F): 40 mm Hg (approximately)

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): 0.012

8. Evaporation rate (butyl acetate = 1): Greater than 1

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Reacts with chemically active metals such as sodium, potassium, and beryllium, or with powdered magnesium, aluminum, and zinc.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, hydrogen fluoride, and carbon monoxide) may be released when 1,1,1,2-tetrachloro-2,2-difluoroethane decomposes.

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

• **Flammability**

1. Not combustible

• **Warning properties**

No quantitative data are available relating warning properties to air concentrations of of this compound. Therefore, for the purposes of this guideline, it is treated as a material with poor warning properties.

1,1,1,2-Tetrachloro-2,2-difluoroethane 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 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 1,1,1,2-tetrachloro-2,2-difluoroethane may be used. An analytical method for 1,1,1,2-tetrachloro-2,2-difluoroethane 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 or solid 1,1,1,2-tetrachloro-2,2-difluoroethane.

• Non-impervious clothing which becomes contaminated with liquid or solid 1,1,1,2-tetrachloro-2,2-difluoroethane should be removed promptly and not reworn until the 1,1,1,2-tetrachloro-2,2-difluoroethane is removed from the clothing.

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

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in dry cleaning industry for wool, cotton, dacron, and leather materials in combination with other solvents as azeotropic mixture; use in electric or electronic industries for cleaning rosin fluxes from circuit boards, and cleaning solvent for complex electronic parts and magnetic tapes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer and plastics industry as blowing or foaming agent for cellular and microporous materials	Local exhaust ventilation
Use as solvent extractant for separation and purification of biological material; use as a dye solvent to give brighter colors, and to detect surface cracks or defects in metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as corrosion inhibitors in brake fluid, surface coatings on electrical equipment, heat control of reactions, and propellants	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 1,1,1,2-tetrachloro-2,2-difluoroethane 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 1,1,1,2-tetrachloro-2,2-difluoroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,1,2-tetrachloro-2,2-difluoroethane 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 1,1,1,2-tetrachloro-2,2-difluoroethane, 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 1,1,1,2-tetrachloro-2,2-difluoroethane 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 1,1,1,2-tetrachloro-2,2-difluoroethane 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.

• Waste disposal methods:

1,1,1,2-Tetrachloro-2,2-difluoroethane may be disposed of:

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

REFERENCES

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

• Clayton, J. W.: "Toxicity Studies on 1,1,2,2-Tetrachloro-1,2-Difluoroethane and 1,1,1,2-Tetrachloro-2,2-Difluoroethane," *American Industrial Hygiene Association Journal*, 27:332-340, 1966.

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• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
5000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
15,000 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 15,000 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 1,1,2,2-Tetrachloro-1,2-Difluoroethane*

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-CCl_2F
- Synonyms: Refrigerant 112; halocarbon 112
- Appearance and odor: Colorless liquid or solid with a slight ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2,2-tetrachloro-1,2-difluoroethane is 500 parts of 1,1,2,2-tetrachloro-1,2-difluoroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 4170 milligrams of 1,1,2,2-tetrachloro-1,2-difluoroethane per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2,2-Tetrachloro-1,2-difluoroethane 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: 1,1,2,2-Tetrachloro-1,2-difluoroethane might cause irritation of the skin and eyes. It might also cause drowsiness and difficult breathing.
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 1,1,2,2-tetrachloro-1,2-difluoroethane.

- **Recommended medical surveillance**

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

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

1,1,2,2-Tetrachloro-1,2-difluoroethane vapor is a narcotic. Rats exposed to 10,000 ppm for 1-½ to 2 hours showed signs of intoxication; concentrations of 20,000 to 30,000 ppm for the same period were fatal and caused pulmonary hemmorhages. In rats repeatedly exposed for 6 hours to 1,000 ppm, there were no clinical signs of toxicity; some showed slight changes in liver cells, and a few female rats had a decreased leukocyte count. The liquid applied to the intact skin of guinea pigs produced mild irritation in 24 hours. Instilled in the eyes of rabbits, it produced mild conjunctival irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 203.8
2. Boiling point (760 mm Hg): 92.8 C (199 F)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of 1,1,2,2-tetrachloro-1,2-difluoroethane): 7
5. Melting point: 26 C (79 F)
6. Vapor pressure at 20 C (68 F): 40 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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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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

7. Solubility in water, g/100 g water at 20 C (68 F): 0.012

8. Evaporation rate (butyl acetate = 1): Greater than 1

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Reacts with chemically active metals such as sodium, potassium, and beryllium, or with powdered aluminum, zinc, and magnesium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, hydrogen fluoride, and carbon monoxide) may be released when 1,1,2,2-tetrachloro-1,2-difluoroethane decomposes.

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

• **Flammability**

1. Not combustible

• **Warning properties**

No quantitative data are available relating warning properties of 1,1,2,2-tetrachloro-1,2-difluoroethane to its air concentrations. Therefore, this compound is treated as a material with poor warning properties. Deichmann and Gerarde report that 1,1,2,2-tetrachloro-1,2-difluoroethane is mildly irritating to rabbit eyes, but the levels at which irritation occurs are not given.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of 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 1,1,2,2-tetrachloro-1,2-difluoroethane may be used. An analytical method for 1,1,2,2-tetrachloro-1,2-difluoroethane 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).

(order number PB 265 028).

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 1,1,2,2-tetrachloro-1,2-difluoroethane.

• Non-impervious clothing which becomes wet with liquid 1,1,2,2-tetrachloro-1,2-difluoroethane or contaminated with solid 1,1,2,2-tetrachloro-1,2-difluoroethane should be removed promptly and not reworn until the 1,1,2,2-tetrachloro-1,2-difluoroethane is removed from the clothing.

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

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in dry cleaning industry for wool, cotton, dacron, and leather materials in combination with other solvents as azeotropic mixture; use in electric or electronic industries for cleaning rosin fluxes from circuit boards, and cleaning solvent for complex electronic parts and magnetic tapes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in polymer and plastics industry as blowing or foaming agent for cellular and microporous materials	Local exhaust ventilation
Use as solvent extractant for separation and purification of biological material; use as a dye solvent to give brighter colors, and to detect surface cracks or defects in metals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as corrosion inhibitors in brake fluid, surface coatings on electrical equipment, heat control of reactions, and propellants	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 1,1,2,2-tetrachloro-1,2-difluoroethane 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 1,1,2,2-tetrachloro-1,2-difluoroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2,2-tetrachloro-1,2-difluoroethane 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 1,1,2,2-tetrachloro-1,2-difluoroethane, 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 1,1,2,2-tetrachloro-1,2-difluoroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the person to vomit by having him touch the back of the throat with his finger or by giving him large amounts (one pint or more) of warm salt water (two tablespoons of salt per pint of water.) Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

• If 1,1,2,2-tetrachloro-1,2-difluoroethane 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.

• Waste disposal methods:

1,1,2,2-Tetrachloro-1,2-difluoroethane 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.

REFERENCES

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

• Clayton, J. W., et al.: "Toxicity Studies on 1,1,2,2-

Tetrachloro-1,2-Difluoroethane and 1,1,1,2-Tetrachloro-2,2-Difluoroethane," *American Industrial Hygiene Association Journal*, 27:332-340, 1960.

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• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

* SPECIAL NOTE

1,1,2,2-Tetrachloro-1,2-difluoroethane 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 20, 1979.

RESPIRATORY PROTECTION FOR 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
5000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
15,000 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 15,000 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 1,1,2,2-Tetrachloroethane

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: $CHCl_2CHCl_2$
- Synonyms: Symmetrical-tetrachloroethane; acetylene tetrachloride; sym-tetrachlorethane
- Appearance and odor: Colorless or pale yellow liquid with a sickly sweet odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2,2-tetrachloroethane is 5 parts of 1,1,2,2-tetrachloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of 1,1,2,2-tetrachloroethane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 1 ppm (6.87 mg/m^3) averaged over a 10-hour work shift. The NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2,2-Tetrachloroethane 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: Breathing in high concentrations of 1,1,2,2-tetrachloroethane may cause irritation of the eyes and nose, nausea, vomiting, and drowsiness. Liver and kidney damage may occur. If the exposure was severe, within a few hours a deep dusky coloration of the skin may appear, followed by unconsciousness and death. If the exposed worker is removed immediately, he may recover completely but should be placed under observation in case late symptoms appear. If the vapor or liquid of 1,1,2,2-tetrachloroethane gets into the eyes, it may cause watering and burning. It may cause serious eye damage unless immediate medical care is obtained.

2. Long-term Exposure: Prolonged or repeated exposure to 1,1,2,2-tetrachloroethane, either by breathing or by absorbing it through the skin, may cause fatigue, loss of appetite, tremors, weight loss, constipation, heart damage, blood changes, kidney damage, abdominal distress or pain, vomiting, dizziness, tenderness, liver damage with such symptoms as pain over the liver, dark urine, and yellow jaundice. Reproductive abnormalities have been noted in studies of animals following exposure to high levels of 1,1,2,2-tetrachloroethane. Prolonged or repeated skin contact with 1,1,2,2-tetrachloroethane may also 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 1,1,2,2-tetrachloroethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,1,2,2-tetrachloroethane 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 central nervous system should be stressed.

—Liver function tests: 1,1,2,2-Tetrachloroethane causes liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

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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—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

1,1,2,2-Tetrachloroethane is highly toxic to the liver and is a central nervous system depressant. Rats exposed to 500 ppm for 4 hours survived, but 1,000 ppm was fatal. Reports of industrial experience indicate that cases of mild intoxication have presented symptoms of gastrointestinal irritation (nausea, vomiting, abdominal pain, anorexia) and central nervous system effects (dizziness, headache, irritability, nervousness, insomnia); more severe exposure resulted in liver involvement (enlarged and tender liver, jaundice, bilirubinuria), nephritis (albuminuria and casts); and tremors of hands and eyelids. In cases of severe industrial intoxication, there was hepatic necrosis with jaundice, sometimes progressing to cirrhosis; individuals who died during the acute stage also showed cerebral edema and pulmonary edema with hemorrhage, as well as liver and kidney injury. One study reported that human subjects exposed to 335 ppm for 10 minutes or 186 ppm for 30 minutes noted a disagreeable odor; there were some upper respiratory irritation and central nervous system effects. Among a group of workers in India exposed to 20-65 ppm there was nausea, vomiting, and abdominal pain and a high incidence of tremor of the hands. Prolonged skin exposure may be expected to produce dermatitis due to defatting action. Eye damage has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 167.8
2. Boiling point (760 mm Hg): 146 C (295 F)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of 1,1,2,2-tetrachloroethane): 5.8
5. Melting point: −42.5 C (−44.5 F)
6. Vapor pressure at 20 C (68 F): 8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.29
8. Evaporation rate (butyl acetate = 1): 0.65

• **Reactivity**

1. Conditions contributing to instability: Heat; unusual exposure to light in the presence of air may form small amounts of phosgene.
2. Incompatibilities: Reacts with chemically active metals or with strong caustics. In the presence of steam, contact with hot iron, aluminum, and zinc may cause formation of toxic vapors.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, hydrogen chloride, chlorinated solvents, and carbon monoxide) may be released when 1,1,2,2-tetrachloroethane decomposes.
4. Special precautions: Liquid 1,1,2,2-tetrachloroethane will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Patty states that the odor of 1,1,2,2-tetrachloroethane is detectable at 5 ppm (3 ppm, according to Lehmann). Since the odor threshold is at (or below) the permissible exposure limit, this compound is treated as a material with good warning properties.

Grant indicates that this compound is not 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 1,1,2,2-tetrachloroethane may be used. An analytical method for 1,1,2,2-tetrachloroethane 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).

PB 265 028).

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 tc 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 1,1,2,2-tetrachloroethane.

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

• Where exposure of an employee's body to liquid 1,1,2,2-tetrachloroethane 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 1,1,2,2-tetrachloroethane should be removed immediately and not reworn until the 1,1,2,2-tetrachloroethane 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 1,1,2,2-tetrachloroethane contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid 1,1,2,2-tetrachloroethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

• Eating and smoking should not be permitted in areas where liquid 1,1,2,2-tetrachloroethane is handled, processed, or stored.

• Employees who handle liquid 1,1,2,2-tetrachloroethane 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 1,1,2,2-tetrachloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chemical intermediate in manufacture of tetrachloroethylene and trichloroethylene; use in cleaning and extraction processes; use in chlorination of phthalic anhydride; use in manufacture of cyanogen chloride, polymers, and tetrachloro-alkylphenol	Local exhaust ventilation; general dilution ventilation
Use as a fumigant in greenhouses	Personal protective equipment
Use in manufacture of lacquers and varnishes, paint and varnish removers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use and preparation of insecticides and weed killers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in cleaning and degreasing of metals	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a solvent in preparation of adhesives	Local exhaust ventilation
Use during addition to aliphatic alcohols and acetates to improve solvency for nitrocellulose and cellulose acetate as in photographic film	Local exhaust ventilation
Use in application of adhesives	General dilution ventilation; personal protective equipment
Use in refining of waxes and resins	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 1,1,2,2-tetrachloroethane 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 1,1,2,2-tetrachloroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2,2-tetrachloroethane 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 1,1,2,2-tetrachloroethane, 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 1,1,2,2-tetrachloroethane 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 1,1,2,2-tetrachloroethane 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:

1,1,2,2-Tetrachloroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on 1,1,2,2-tetrachloroethane, look up 1,1,2,2-tetrachloroethane in the following documents:

• Medical Surveillance for Chemical Hazards
• Respiratory Protection for Chemical Hazards
• Personal Protection and Sanitation for Chemical Hazards
• NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane (December 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR 1,1,2,2-TETRACHLOROETHANE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
150 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 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 Health Guideline for Tetrachloroethylene*

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: $CCl_2 = CCl_2$
- Synonyms: Perchloroethylene; perchlorethylene; tetrachlorethylene; perk
- Appearance and odor: Colorless liquid with an odor like chloroform or ether.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetrachloroethylene is 100 parts of tetrachloroethylene 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. NIOSH has recommended that the permissible exposure limit be reduced to 50 ppm (339 mg/m³) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 100 ppm (678 mg/m³) averaged over a 15-minute period. The NIOSH Criteria Document for Tetrachloroethylene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetrachloroethylene 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: Tetrachloroethylene may cause headache, nausea, drowsiness, dizziness, incoordination, and unconsciousness. It may also cause irritation of the eyes, nose, and throat and flushing of the face and neck. In addition, it might cause liver damage with such findings as yellow jaundice and dark urine. The liver damage may become evident several weeks after the exposure.

2. Long-term Exposure: Prolonged or repeated overexposure to liquid tetrachloroethylene may cause irritation of the skin. It might also cause damage to the liver and kidneys.

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 tetrachloroethylene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetrachloroethylene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and the cardiovascular and neurological systems should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Tetrachloroethylene 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 also been observed from exposure, a urinalysis should be obtained to include at 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**

Tetrachloroethylene vapor is a narcotic. Rats did not survive when exposed for longer than 12-18 minutes to 12,000 ppm; when exposed repeatedly to 470 ppm they showed liver and kidney injury. Cardiac arrhythmias

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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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attributed to sensitization of the myocardium to epinephrine have been observed with certain other chlorinated hydrocarbons, but exposure of dogs to concentrations of 5000 and 10,000 ppm tetrachloroethylene did not produce this phenomenon. Four human subjects were unable to tolerate 5000 ppm in a chamber for 6 minutes. They experienced vertigo, nausea, and mental confusion during the 10 minutes following cessation of exposure. In an industrial exposure to an average concentration of 275 ppm for 3 hours, followed by 1100 ppm for 30 minutes, a worker lost consciousness; there was apparent clinical recovery 1 hour after exposure but the monitored concentration of tetrachloroethylene in the patient's expired air diminished slowly over a 2-week period. Long-term industrial exposures have been reported to cause various neuropathies, such as numbness, trembling, neuritis, and defects of memory. During the second and third post-exposure weeks, the results of liver function tests became abnormal, suggesting that acute exposure had had a significant effect upon the liver. Other instances of liver injury following industrial exposure have been reported. Other effects on humans of inhalation of various concentrations are as follows: 2000 ppm, mild narcosis within 5 minutes; 600 ppm, sensation of numbness around the mouth, dizziness, and some incoordination after 10 minutes. In human experiments, 7-hour exposures at 100 ppm resulted in mild irritation of the eyes, nose, and throat; flushing of the face and neck; headache; somnolence; and slurred speech. Exposure of the skin to the liquid for 40 minutes resulted in a progressively severe burning sensation beginning within 5 to 10 minutes; the result was marked erythema, which subsided after 1 to 2 hours. The liquid sprayed into rabbits' eyes produced immediate pain and blepharospasm; patches of epithelium were lost, but the eyes recovered completely within 2 days.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 165.85
2. Boiling point (760 mm Hg): 121.2 C (250 F)
3. Specific gravity (water = 1): 1.62
4. Vapor density (air = 1 at boiling point of tetrachloroethylene): 5.83
5. Melting point: −22.4 C (−8 F)
6. Vapor pressure at 20 C (68 F): 14 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
8. Evaporation rate (butyl acetate = 1): 2.8

- **Reactivity**

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Tetrachloroethylene reacts with strong oxidizers and chemically active metals such as barium, lithium, and beryllium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released when tetrachloroethylene decomposes.
4. Special precautions: Liquid tetrachloroethylene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Both May and Stern state that 50 ppm is the odor threshold for tetrachloroethylene.
2. Eye Irritation Level: Grant reports that "exposure to high concentrations of (tetrachloroethylene) vapor causes mild sensation of irritation to the eyes, but serious injury is not likely." The exact concentrations producing irritation are not mentioned by Grant.

Spector, however, reports that after a 20- to 30-minute exposure to 206 to 235 ppm, eye irritation occurs in humans.

Patty reports "very slight irritation of the eyes" among humans at 106 ppm.

3. Other Information: Spector reports that a 10-minute exposure to 513 to 690 ppm produces nose and throat irritation.
4. Evaluation of Warning Properties: Since the odor threshold of tetrachloroethylene is below the permissible exposure limit, and since eye irritation occurs at a concentration only twice the permissible exposure limit, its warning properties are considered to be adequate.

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 tetrachloroethylene. 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 tetrachloroethylene. 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 tetrachloroethylene may be used. An analytical method for tetrachloroethylene 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 tetrachloroethylene.

• Non-impervious clothing which becomes contaminated with liquid tetrachloroethylene should be removed promptly and not reworn until the tetrachloroethylene is removed from the clothing.

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

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

SANITATION

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

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

Operation	Controls
Use as dry cleaning solvent; as degreasing and metal cleaning agent; in vapor degreasing of metal parts	Local exhaust ventilation; general dilution; personal protective equipment
Use as chemical intermediate in production of fluorocarbons, pesticides, and trichloroacetic acid	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as scouring, sizing, desizing, solvent and greaser remover in processing and finishing of textiles	Local exhaust ventilation; general dilution; personal protective equipment
Use as general industrial solvent in rubber, textile, printing, soap, and paint remover industries	Local exhaust ventilation; general dilution; personal protective equipment
Use as extraction agent for vegetable and mineral oils and in pharmaceutical industry; as vermifuge; as laundry treatment for presoaking and as drying medium in metal and wood industries	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 tetrachloroethylene 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 tetrachloroethylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tetrachloroethylene 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 tetrachloroethylene, 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 tetrachloroethylene 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 tetrachloroethylene 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:

Tetrachloroethylene 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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* SPECIAL NOTE

Tetrachloroethylene 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 20, 1979.

RESPIRATORY PROTECTION FOR TETRACHLOROETHYLENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
	A gas mask with a chin-style or a front- or back-mounted organic vapor canister.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
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.

PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600

DEFINITION: aerosol collected by sampler with 4-µm median cut point

CAS: None RTECS: None

METHOD: 0600, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 3: 15 January 1998

OSHA : 5 mg/m^3
NIOSH: no REL
ACGIH: 3 mg/m^3

PROPERTIES: contains no asbestos and quartz less than 1%; penetrates non-ciliated portions of respiratory system

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell [HD] cyclone, or Aluminum cyclone + tared 5-µm PVC membrane)

FLOW RATE: nylon cyclone: 1.7 L/min
HD cyclone: 2.2 L/min
Al cyclone: 2.5 L/min

VOL-MIN: 20 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 10 mg/m^3 (lab and field)

BIAS: dependent on dust size distribution [1]

OVERALL PRECISION ($\hat{S}_{rT}$): dependent on size distribution [1,2]

ACCURACY: dependent on size distribution [1]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

ANALYTE: mass of respirable dust fraction

BALANCE: 0.001 mg sensitivity; use same balance before and after sample collection

CALIBRATION: National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights

RANGE: 0.1 to 2 mg per sample

ESTIMATED LOD: 0.03 mg per sample

PRECISION: <10 µg with 0.001 mg sensitivity balance; <70 µg with 0.01 mg sensitivity balance [3]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 200-L air sample. The method measures the mass concentration of any non-volatile respirable dust. In addition to inert dusts [4], the method has been recommended for respirable coal dust. The method is biased in light of the recently adopted international definition of respirable dust, e.g., ≈ +7% bias for non-diesel, coal mine dust [5].

INTERFERENCES: Larger than respirable particles (over 10 µm) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in samples are known to be caused by inverting the cyclone assembly. Heavy dust loadings, fibers, and water-saturated dusts also interfere with the cyclone's size-selective properties. The use of conductive samplers is recommended to minimize particle charge effects.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

EQUIPMENT:

1. Sampler:
   a. Filter: 5.0-µm pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported by a cassette filter holder (preferably conductive).
   b. Cyclone: 10-mm nylon(Mine Safety Appliance Co., Instrument Division, P. O. Box 427, Pittsburgh, PA 15230), Higgins-Dewell(BGI Inc., 58 Guinan St., Waltham, MA 02154)[7], aluminum cyclone (SKC Inc., 863 Valley View Road, Eighty Four, PA 15330), or equivalent.
2. Personal sampling pump, 1.7 L/min ± 5% for nylon cyclone, 2.2 L/min ± 5% for HD cyclone, or 2.5 L/min ± 5% for the Al cyclone with flexible connecting tubing.
   NOTE: Pulsation in the pump flow must be within ± 20% of the mean flow.
3. Balance, analytical, with sensitivity of 0.001 mg.
4. Weights, NIST Class S-1.1, or ASTM Class 1.
5. Static neutralizer, e.g., Po-210; replace nine months after the production date.
6. Forceps (preferably nylon).
7. Environmental chamber or room for balance, e.g., 20°C ± 1 °C and 50% ± 5% RH.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
2. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps (nylon forceps if further analyses will be done).
   c. Pass the filter over an anti-static radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
3. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette.
4. Remove the cyclone's grit cap before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone may be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
5. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

6. Calibrate each personal sampling pump to the appropriate flow rate with a representative sampler in line.
   NOTE 1: Because of their inlet designs, nylon and aluminum cyclones are calibrated within a large vessel with inlet and outlet ports. The inlet is connected to a calibrator (e.g., a bubble meter). The cyclone outlet is connected to the outlet port within the vessel, and the vessel outlet is attached to the pump. See APPENDIX for alternate calibration procedure. (The calibrator can be connected directly to the HD cyclone.)
   NOTE 2: Even if the flowrate shifts by a known amount between calibration and use, the nominal flowrates are used for concentration calculation because of a self-correction feature of the cyclones.
7. Sample 45 min to 8 h. Do not exceed 2 mg dust loading on the filter. Take 2 to 4 replicate samples for each batch of field samples for quality assurance on the sampling procedure (see Step 10).
   NOTE : Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in an environmentally controlled area or chamber.

CALIBRATION AND QUALITY CONTROL:

9. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
10. The set of replicate field samples should be exposed to the same dust environment, either in a laboratory dust chamber [8] or in the field [9]. The quality control samples must be taken with the same equipment, procedures, and personnel used in the routine field samples. Calculate precision from these replicates and record relative standard deviation (S_r) on control charts. Take corrective action when the precision is out of control [8].

MEASUREMENT:

11. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloading, leakage, wet, torn, etc.).

CALCULATIONS:

12. Calculate the concentration of respirable particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \cdot 10^3, \; mg/m^3$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B_1 = mean tare weight of blank filters (mg).
B_2 = mean post-sampling weight of blank filters (mg)
V = volume as sampled at the nominal flowrate (i.e., 1.7 L/min or 2.2 L/min)

EVALUATION OF METHOD:

1. Bias: In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust convention. The theory for calculating bias was developed by Bartley and Breuer [10]. For this method, the bias, therefore, depends on the international convention for respirable dust, the cyclones' penetration curves, and the size distribution of the ambient dust. Based on measured penetration curves for non-pulsating flow [1], the bias in this method is shown in Figure 1.

   For dust size distributions in the shaded region, the bias in this method lies within the ± 0.10 criterion established by NIOSH for method validation. Bias larger than ± 0.10 would, therefore, be expected for some workplace aerosols. However, bias within ± 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

   Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [12] showed that cyclone samples with pulsating flow can have negative bias as large as −0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias magnitude is less than 0.02 for most dust size distributions encountered in the workplace.

   Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [13] have found

electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem. Use of conductive samplers and filter cassettes(Omega Specialty Instrument Co., 4 Kidder Road, Chelmsford, MA 01824) is recommended.

2. Precision: The figure 0.068 mg quoted above for the precision is based on a study [3] of weighing procedures employed in the past by the Mine Safety and Health Administration (MSHA) in which filters are pre-weighed by the filter manufacturer and post-weighed by MSHA using balances readable to 0.010 mg. MSHA [14] has recently completed a study using a 0.001 mg balance for the post-weighing, indicating imprecision equal to 0.006 mg.

   Imprecision equal to 0.010 mg was used for estimating the LOD and is based on specific suggestions [8] regarding filter weighing using a single 0.001 mg balance. This value is consistent with another study [15] of repeat filter weighings, although the actual attainable precision may depend strongly on the specific environment to which the filters are exposed between the two weighings.

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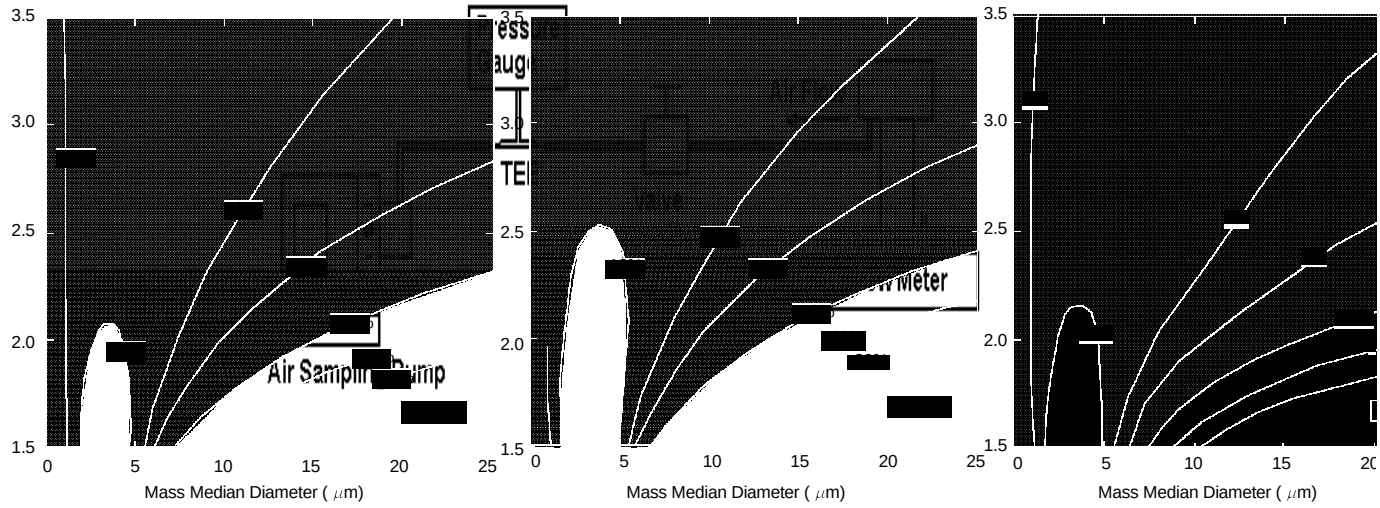
METHOD REVISED BY: David L. Bartley, Ph.D., NIOSH/DPSE/ARDB and Ray Feldman, OSHA.



10-mm nylon cyclone at 1.7 L/min Higgins-Dewell cyclone at 2.2 L/min Aluminum cyclone at 2.5 L/m

Figure 1. Bias of three cyclone types relative to the international respirable dust samp convention.

APPENDIX: Jarless Method for Calibration of Cyclone Assemblies

This procedure may be used in the field to calibrate an air sampling pump and a cyclone assembly without using the one-liter "calibration jar".

(1) Connect the pump to a pressure gauge or water manometer and a light load (adjustable valve or 5-µm filter) equal to 2" to 5" H_2O with a "TEE" connector and flexible tubing. Connect other end of valve to an electronic bubble meter or standard bubble tube with flexible tubing (See Fig. 2.1).
NOTE: A light load can be a 5-µm filter and/or an adjustable valve. A heavy load can be several 0.8-µm filters and/or adjustable valve.

(2) Adjust the pump to 1.7 L/min, as indicated on the bubble meter/tube, under the light load conditions (2" to 5" H_2O) as indicated on the pressure gauge or manometer.

(3) Increase the load until the pressure gauge or water manometer indicates between 25" and 35" H_2O. Check the flow rate of the pump again. The flow rate should remain at 1.7 L/min ± 5%.

(4) Replace the pressure gauge or water manometer and the electronic bubble meter or standard bubble tube with the cyclone having a clean filter installed (Fig. 2.2). If the loading caused by the cyclone assembly is between 2" and 5" H_2O, the calibration is complete and the pump and cyclone are ready for sampling.

Figure 2.1 Block Diagram of Pump/Load/Flow Meter Set-up.

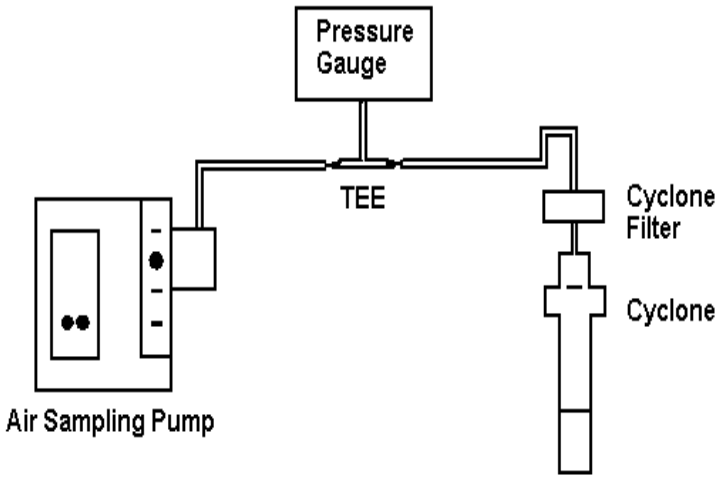


Figure 2.2. Block Diagram with Cyclone as the Test Load.

Occupational Health Guideline for Tetraethyl Lead

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: $Pb(C_2H_5)_4$
- Synonyms: TEL; lead tetraethyl; motor fuel antiknock compound
- Appearance and odor: Colorless liquid (or dyed red, orange, or blue) with a slight musty odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetraethyl lead is 0.075 milligrams of tetraethyl lead per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended that the permissible exposure limit be changed to 0.1 mg/m^3. The American Conference of Governmental Industrial Hygienists has recommended for tetraethyl lead a Threshold Limit Value of 0.1 mg/m^3 with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetraethyl lead 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**

The absorption by humans of a sufficient quantity of tetraethyl lead either briefly at a high rate or for prolonged periods at a lower rate may cause intoxication. The onset of symptoms may be delayed for up to eight days after termination of exposure. The milder toxic effects are difficulty in sleeping, tiredness, wild dreams, anxiety, trembling, spasms, slow heart beat, low body temperature, paleness, nausea and loss of appetite. More severe intoxication causes episodes of disorientation, hallucinations, grimacing, and intense activity which requires that the person be restrained. These episodes may convert into manic or violent convulsive seizures which may end in unconsciousness or death. Tetraethyl lead may cause irritation of the eyes. Fetal damage may occur from exposure of the mother to tetraethyl lead, by analogy to methyl mercury.

- **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 tetraethyl lead.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetraethyl lead 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 mental disorders or hypotension would be expected to be at increased risk from exposure. Examination of the central nervous system and the cardiovascular system should be stressed.

—Urinalysis: Normal kidney function is considered necessary for biologic monitoring. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The concentration of lead should be determined. Urine specimens with a specific gravity less than 1.020 should be discarded and another sampled obtained.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that the determination of lead in the urine should be repeated quarterly.

- **Summary of toxicology**

Tetraethyl lead vapor affects the nervous system 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.

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

causes mental aberrations including psychosis, mania, and convulsions. Of 41 female Swiss mice which survived for 36 weeks after a single subcutaneous injection of 0.6 mg, 5 developed malignant lymphomas during the next 15 weeks; the significance of these data cannot be evaluated, because this tumor occurs spontaneously with a variable incidence in the mouse strain used. The absorption by humans of a sufficient quantity of tetraethyl lead, either briefly at a high rate (100 mg/m^3 for 1 hour) or for prolonged periods at a lower rate, causes acute intoxication; chronic intoxication has not been observed. The onset of symptoms may be delayed for up to 8 days after termination of exposure. The milder manifestations of intoxication are insomnia, lassitude, lurid dreams, dream-like waking states of anxiety, tremor, hyperreflexia, spasmodic muscular contractions, bradycardia, hypotension, hypothermia, pallor, nausea, and anorexia. More severe intoxication causes recurrent or nearly continuous episodes of disorientation, hallucinations, facial contortions, and intense hyperactivity which requires that the individual be restrained. Such episodes may convert abruptly into manic or violent convulsive seizures which may terminate in coma and death. During intoxication there is a striking elevation of the rate of excretion of lead in the urine but only a negligible or slight elevation of the concentration of lead in the blood. In severe intoxication, the urine lead is rarely less than 350 ug/l of urine, while the blood lead is rarely more than 50 ug/100 g of blood. There is also a total absence of morphological or chemical abnormalities in the erythrocytes, in sharp contrast to intoxication caused by inorganic lead. In a mortality study of 592 workers, the mean exposure time was 17.9 years, and urinary lead levels during this period did not exceed 180 ug/l; the incidence of death in this group and in a control group of employees was less than that expected in the general population, and there were no peculiarities in the specific causes of death in either group. In a similar study of a different cohort of these exposed workers, there were no significant health differences when compared with a control group. Although tetraethyl lead may be irritating to the eyes, this effect is considered insignificant when compared with the effects on the central nervous system.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 323.4
2. Boiling point (760 mm Hg): Decomposes above 100 C (212 F)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of tetraethyl lead): 8.6
5. Melting point: −138 to −130 C (−216 to −202 F)
6. Vapor pressure at 20 C (68 F): 0.2 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: Temperatures above 100 C (212 F) cause decomposition and development of pressure that may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers, such as sulfuryl chloride or potassium permangonate, may cause fires and explosions.
3. Hazardous decomposition products: Toxic airborne substances (such as lead fumes and carbon monoxide) may be released in a fire involving tetraethyl lead.
4. Special precautions: Tetraethyl lead will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 93 C (200 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 tetraethyl lead. The AIHA *Hygienic Guide* states that this substance "has a characteristic sweetish odor, but the intensity of the odor is not adequate to warn of hazardous concentrations."
2. Eye Irritation Level: Grant states that "concerning local effects on the eye from direct contact, there was recorded by Leake in 1926 a strange account of a contamination of the eyes from a splash of gasoline containing tetraethyl lead, after which the patient was said to have been unable to see for three-fourths of an hour. In the course of two months the patient was reported improved and was found to have no corneal or ophthalmoscopic abnormality, but was thought to have slight mydriasis, photophobia, and contraction of the visual field. Very likely the initial difficulty in seeing was due to smarting sensation in the eyes and blepharospasm. The evidence of later eye abnormality in this case seems quite indefinite and questionable.

"I have tested high-test gasoline containing tetraethyl lead by dropping on rabbit eyes, and have found it to cause immediate pain and blepharospasm lasting several minutes. When the application was repeated ten times in the course of five minutes under local anesthesia, it produced conjunctival hyperemia and moderate flocculent discharge, but no damage to cornea or conjunctiva."

3. Evaluation of Warning Properties: Since there is no quantitative information relating warning properties to air concentrations of tetraethyl lead, 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 tetraethyl lead 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 undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon).

• Clothing contaminated with undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon) should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetraethyl lead from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetraethyl lead, the person performing the operation should be informed of tetraethyl lead's hazardous properties.

• If employees' clothing has had any possibility of being contaminated with undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon), employees should change into uncontaminated clothing before leaving the work premises.

• Non-impervious clothing which becomes contaminated with undiluted liquid tetraethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon) should be removed immediately and not reworn until the tetraethyl lead is removed from the clothing.

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during manufacture in preparation of antiknock agents for fuels	Process enclsoure; local exhaust ventilation; personal protective equipment
Liberation during formulation at petroleum refinery for use as an antiknock agent	Local exhaust ventilation; total enclosure; personal protective devices

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 tetraethyl lead or strong concentrations of tetraethyl lead 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 tetraethyl lead or strong concentrations of tetraethyl lead vapors get on the skin, immediately rinse the contaminated skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. If liquid tetraethyl lead or strong concentrations of tetraethyl lead vapors penetrate through the clothing, remove the clothing immediately and first rinse the skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of tetraethyl lead, 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 tetraethyl lead 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 tetraethyl lead 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:

Tetraethyl lead 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 TETRAETHYL LEAD

Condition	Minimum Respiratory Protection* Required Above 0.075 mg/m³
Vapor Concentration	
0.75 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3.75 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any 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 tetraethyl lead; 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 40 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for Tetrahydrofuran

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_8O
- Synonyms: Diethylene oxide; tetramethylene oxide; THF
- Appearance and odor: Colorless liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetrahydrofuran is 200 parts of tetrahydrofuran per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 590 milligrams of tetrahydrofuran per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetrahydrofuran 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 tetrahydrofuran may cause irritation of the eyes and nose, nausea, dizziness, and headache.

2. Long-term Exposure: Prolonged or repeated exposure to tetrahydrofuran may cause drying 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 tetrahydrofuran.

- **Recommended medical surveillance**

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

—Skin disease: Tetrahydrofuran 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 tetrahydrofuran 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 tetrahydrofuran 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 tetrahydrofuran 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**

Tetrahydrofuran is an anesthetic agent and a mild upper respiratory tract irritant. Exposure of animals to vapor above 3000 ppm for 8 hours daily for 20 days produced irritation of the upper respiratory tract. Some injury to the liver and kidneys was observed, which was possibly due to impurities, since other studies have not confirmed this finding. Concentrations above 25,000 ppm produced anesthesia, with a small margin of safety between anesthesia and death. Severe headaches were

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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noted among technicians performing this experiment. Daily 6-hour exposures of dogs for 3 to 4 weeks at 200 ppm produced only a slight change in pulse pressure, but no other signs were noted, even when continued for a total of 9 weeks followed by an additional 3 weeks' exposure at nearly 400 ppm. This substance was irritating to the skin of rabbits when applied in aqueous solutions exceeding 20% concentration, although it has not been observed to be a significant skin irritant or sensitizer in industrial practice. No chronic systemic effects have been reported in humans, although nausea, dizziness, and headaches are said to occur with overexposure and are readily reversible in fresh air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 72
2. Boiling point (760 mm Hg): 66 C (151 F)
3. Specific gravity (water = 1): 0.9
4. Vapor density (air = 1 at boiling point of tetrahydrofuran): 2.5
5. Melting point: −108 C (−163 F)
6. Vapor pressure at 20 C (68 F): 145 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): 14.5

- **Reactivity**

1. Conditions contributing to instability: Heat and 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 tetrahydrofuran.
4. Special precautions: Tetrahydrofuran will attack some forms of plastics, rubber, and coatings. Storage in the presence of air and light causes the formation of explosive peroxides that remain dissolved in tetrahydrofuran. Containers may explode when their caps or stoppers are removed.

- **Flammability**

1. Flash point: −14.5 C (6 F) (closed cup)
2. Autoignition temperature: 321 C (610 F)
3. Flammable limits in air, % by volume: Lower: 2; Upper: 11.8
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: May and Summer both report an odor threshold for tetrahydrofuran of 30 ppm.
2. Eye Irritation Level: Sax reports that tetrahydrofuran is an eye irritant, and Stecher, Browning, and the ILO indicate that it is a mucous membrane irritant, but the concentrations which produce irritation are not given. The *Handbook of Organic Industrial Solvents* reports that tetrahydrofuran "may cause irritation to mucuous membranes at concentrations higher than the threshold limit," but no quantitative information is available concerning the threshold of eye irritation.
3. Other Information: "The TLV of 200 ppm is recommended to protect against irritative effects and has a wide margin of safety for narcotic and systemic effects," according to the *Documentation of TLV's.*
4. Evaluation of Warning Properties: Since the odor threshold of tetrahydrofuran is well 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 tetrahydrofuran 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 tetrahydrofuran may be used. An analytical method for tetrahydrofuran 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 tetrahydrofuran.

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

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

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

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as a solvent in preparation of printing inks, adhesives, lacquers, and other coatings	General dilution ventilation; personal protective equipment
Use as a Grignard reagent in synthesis of motor fuels, vitamins, hormones, pharmaceuticals, synthetic perfumes, organometallic compounds and insecticides	General dilution ventilation; process enclosure; personal protective equipment
Use as an intermediate in the preparation of various chemicals, including adipic acid, butadiene, polytetramethylene, and acrylic acid	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 tetrahydrofuran 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 tetrahydrofuran gets on the skin, promptly wash the contaminated skin with water. If tetrahydrofuran 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 tetrahydrofuran, 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 tetrahydrofuran 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 tetrahydrofuran 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. Tetrahydrofuran should

not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Tetrahydrofuran 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: "Tetrahydrofuran," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR TETRAHYDROFURAN

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).
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.
20,000 ppm or less	A powered air-purifying respirator with a full facepiece and organic vapor cartridge(s). 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 20,000 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 Tetramethyl Lead

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: $Pb(CH_3)_4$
- Synonyms: TML; lead tetramethyl; motor fuel antiknock compound
- Appearance and odor: Colorless liquid (or dyed red, orange, or blue) with a slight musty odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetramethyl lead is 0.075 milligram of tetramethyl lead 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 tetramethyl lead a Threshold Limit Value of 0.150 mg/m^3 with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetramethyl lead 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**

Although there have been no reports of human intoxication from tetramethyl lead exposure, animal experiments suggest that tetramethyl lead may cause toxic effects similiar to those produced by tetraethyl lead. Tetraethyl lead exposure effects range from difficulty in sleeping, bad dreams, restlessness, anxiety, nausea, and poor appetite to the more severe symptoms of acute mental disturbance characterized by delirium, violent behavior, convulsive seizures, unconsciousness, and death. Fetal damage may occur from exposure of the mother to tetramethyl lead by analogy to methyl mercury.

- **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 tetramethyl lead.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetramethyl lead 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 mental disorders or hypotension would be expected to be at increased risk from exposure. Examination of the central nervous system and the cardiovascular system should be stressed.

—Urinalysis: Normal kidney function is considered necessary for biologic monitoring. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The concentration of lead should be determined. Urine specimens with a specific gravity of less than 1.020 should be discarded and another sample obtained.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that the determination of the concentration of lead in the urine should be repeated quarterly.

- **Summary of toxicology**

Tetramethyl lead affects the central nervous system in animals and causes signs of increased irritability. Oral administration of 108 mg/kg to rats caused some deaths; effects were tremors, marked hyperactivity, and convulsions. Tetramethyl lead intoxication in animals resembles that caused by tetraethyl lead (TEL), a close

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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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homolog; human intoxication from tetramethyl lead has not been described. A description of human intoxication by TEL is given because of the severity of the effects and the likelihood that intoxication by tetramethyl lead would be similar. TEL effects range from insomnia, bad dreams, restlessness, anxiety, hypotension, nausea, and anorexia to the more severe symptoms of acute mental disturbances characterized by delirium, mania, convulsive seizures, and coma, sometimes followed by death.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 267.3
2. Boiling point (760 mm Hg): 110 C (230 F)
3. Specific gravity (water = 1): 1.99
4. Vapor density (air = 1 at boiling point of tetramethyl lead): 6.5
5. Melting point: −30 C (−22 F)
6. Vapor pressure at 20 C (68 F): 22 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: Temperatures above 100 C (212 F) cause decomposition and development of pressure that may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers, such as sulfuryl chloride or potassium permangonate, may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as lead fumes and carbon monoxide) may be released in a fire involving tetramethyl lead.
4. Special precautions: Tetramethyl lead will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 38 C (100 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 tetramethyl lead.
2. Eye Irritation Level: Tetramethyl lead 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 tetramethyl lead, 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 tetramethyl lead 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 undiluted liquid tetramethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon).
- Clothing contaminated with undiluted liquid tetramethyl lead or solutions containing more than 1.06 milliliters liter (4 milliliters per gallon) of tetramethyl lead should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetramethyl lead from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetramethyl lead, the person performing the operation should be informed of tetramethyl lead's hazardous properties.
- Where there is any possibility of exposure of an

employee's body to undiluted liquid tetramethyl lead or solutiocontaining more than 1.06 milliliters per liter (4 milliliters per gallon) of tetramethyl lead, 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 undiluted liquid tetramethyl lead or solutions containing more than 1.06 milliliters per liter (4 milliliters per gallon) of tetramethyl lead should be removed immediately and not reworn until the tetramethyl lead is removed from the clothing.

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during manufacture in preparation of antiknock fluids	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during formulation at petroleum refinery for use as an antiknock fluid; mixed lead alkyls; as substitutes, in whole or in part, for tetraethyl lead in engine gasoline	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 tetramethyl lead or strong concentrations of tetramethyl lead 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 tetramethyl lead or strong concentrations of tetramethyl lead vapors get on the skin, immediately rinse the contaminated skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. If liquid tetramethyl lead or strong concentrations of tetramethyl lead vapors penetrate through the clothing, remove the clothing immediately and first rinse the skin with kerosene or similar petroleum products, if readily available, then wash the skin using soap or mild detergent and water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of tetramethyl lead, 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 tetramethyl lead 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 tetramethyl 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, 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. Tetramethyl lead 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 tetramethyl lead vapors are permitted.

• Waste disposal method:

Tetramethyl lead 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 TETRAMETHYL LEAD

Condition	Minimum Respiratory Protection* Required Above 0.075 mg/m³
Vapor Concentration	
0.7 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
3.5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any 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 tetramethyl lead; 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 40 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

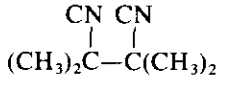
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TETRAMETHYL SUCCINONITRILE

INTRODUCTION

This guideline summarizes pertinent information about tetramethyl succinonitrile (TMSN) 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:** $C_8H_{12}N_2$
- **Structure:**



- **Synonyms:** Succinonitrile tetramethyl, TMSN, TSN, tetramethyl-butanedinitrile
- **Identifiers:** CAS 3333-52-6; RTECS WN4025000; DOT Not assigned
- **Appearance and odor:** Colorless and odorless solid

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 136.22
2. Specific gravity (water = 1): 1.07
3. Melting point: 170°C (338°F), sublimes
4. Insoluble in water

- **Reactivity**

1. Incompatibilities: Strong oxidizers may cause fires and explosions.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., cyanides, oxides of nitrogen, and carbon monoxide) may be released in a fire involving TMSN.

- **Flammability**

1. Extinguishant: Water, dry chemical, or carbon dioxide.
2. Caution: TMSN is a combustible solid. All ignition sources must be controlled when TMSN is used, handled, or stored so as not to create a potential fire or explosion hazard.

- **Warning properties**

Evaluation of warning properties for respirator selection: Based on lack of information on odor threshold and eye irritation levels, TMSN should be considered to have poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for TMSN is 0.5 parts of TMSN per million parts of air (ppm) [3.0 milligrams of TMSN 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 1 ppm (6 mg/m³) as a ceiling concentration determined in any 15-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.5 ppm (3 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 tetramethyl succinonitrile

	Exposure limits ppm	mg/m³
OSHA PEL TWA (Skin)*	0.5	3
NIOSH REL ceiling (15 min)	1	6
ACGIH TLV® TWA (Skin)	0.5	3

* (Skin): Potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

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

- **Summary of toxicology**

Effects on animals: Acute inhalation, subcutaneous injection, or oral administration of TMSN to rats, mice, or hamsters

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produced severe convulsions and death within several hours of exposure.

• **Signs and symptoms of exposure**

Short-term (acute): Exposure to TMSN can cause headache, sensation of pressure within the head, dizziness, nausea, vomiting, peculiar taste, respiratory distress, fatigue, convulsions, and unconsciousness.

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 TMSN, 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 central nervous system.

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to TMSN 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 findings consistent with a convulsant disorder.

• **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 TMSN. 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 central nervous system 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.

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of TMSN. 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 TMSN 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 TMSN may also be used if available. A detailed sampling and analytical method for TMSN may be found in the *NIOSH Manual of Analytical Methods* (method number S155).

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 solid TMSN or liquids containing TMSN.

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

SANITATION

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

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

Skin that becomes contaminated with TMSN 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 TMSN 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 TMSN 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 tetramethyl succinonitrile

Operations	Controls
During the manufacture of polymers initiated by azobisisobutyronitrile; during the processing of products expanded with azobisisobutyronitrile	Local exhaust ventilation
During the manufacture of expanded polyvinyl chloride and polystyrene when azobisisobutyronitrile is used as a blowing agent	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 TMSN, an eye-wash fountain should be provided within the immediate work area for emergency use.

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

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

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 tetramethyl succinonitrile

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 5 ppm	Any supplied-air respirator
	Any self-contained breathing apparatus
Planned or emergency entry into environments containing unknown concentrations or levels above 5 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 1 ppm (6 mg/m^3) (ceiling).

Occupational Health Guideline for Tetranitromethane

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: $C(NO_2)_4$
- Synonyms: Tetan
- Appearance and odor: Colorless to pale yellow liquid or solid. The vapor has a pungent odor and causes tears.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetranitromethane is 1 part of tetranitromethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 8 milligrams of tetranitromethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetranitromethane 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 tetranitromethane may cause irritation of the eyes, upper respiratory tract and skin. It may also cause headaches, fatigue, and drowsiness. After prolonged exposure, the central nervous system and heart may be affected and difficult breathing may occur. Tetranitromethane has been reported to affect the ability of the blood to carry oxygen. This may result in a bluish discoloration of the skin, headache, weakness, irritability, drowsiness, 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 tetranitromethane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetranitromethane 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, eyes, blood, central nervous system, and liver should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Tetranitromethane causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Tetranitromethane is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—A complete blood count: Tetranitromethane has been shown to cause methemoglobinemia in humans. 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 hematrocrit.

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. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Tetranitromethane vapor is a severe irritant of the eyes and respiratory tract. The LC50 for rats was 1230 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 36 minutes; effects were lacrimation, rhinorrhea, gasping, and cyanosis; pulmonary edema was present at autopsy. Repeated exposure to 3.65 ppm for 6 months caused the death of 60% of the rats; at autopsy there were signs of lung infection following acute pneumonitis. In three species of animals, intravenous injection caused methemoglobinemia, anemia, damage to the central nervous system, and edema of the lungs and liver. In workers, various studies showed that exposure caused irritation of the eyes, nose, and throat; dizziness, headache; chest pain, dyspnea; and occasionally skin irritation. Methemoglobinemia is stated to be a systemic effect from human exposure; symptoms result from anoxia and include cyanosis, evident especially in the lips, nose, and earlobes; other effects are weakness, dizziness, and severe headache. Concentrations in excess of 1 ppm will cause lacrimation and upper respiratory irritation, while 0.4 ppm may cause mild irritation. The liquid on the skin may cause mild burns.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 196
2. Boiling point (760 mm Hg): 126 C (259 F)
3. Specific gravity (water = 1): 1.64
4. Vapor density (air = 1 at boiling point of tetranitromethane): 6.8
5. Melting point: 14 C (57 F)
6. Vapor pressure at 20 C (68 F): 8.4 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: Combustible organic matter wet with tetranitromethane may be highly explosive and susceptible to initiation by rather mild shocks.
2. Incompatibilities: Contact with hydrocarbons, alkalies, and metals may form explosive mixtures.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving tetranitromethane or when tetranitromethane decomposes.
4. Special precautions: Tetranitromethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible by itself, but is considered by some to be a weak explosive.

- **Warning properties**

1. Odor Threshold: Patty states that "tetranitromethane can be recognized by its characteristic acrid biting odor." No quantitative information is available, however, concerning its odor threshold.
2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "the irritant property of tetranitromethane may serve as an index to the degree of exposure which can be tolerated, because concentrations in excess of 1 ppm will cause lacrimation and upper respiratory irritation. Concentrations as low as 0.4 ppm may cause mild irritation." Grant states that "the vapors of tetranitromethane are very irritating to the eyes, nose, and respiratory passages. It has been proposed for use as an irritant war gas. Animals are said to show evidence of irritation of the eyes rather quickly at concentrations from 3.3 to 25.2 ppm in air."
3. Evaluation of Warning Properties: Through its irritant effects, tetranitromethane can be detected below the permissible exposure limit. For the purposes of this guideline, therefore, tetranitromethane is treated as a material with good warning properties. It is a strong oxidizer.

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 drawing tetranitromethane through ethyl acetate with subsequent gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure tetranitromethane may be used. An analytical method for tetranitromethane 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 solid or liquid tetranitromethane where skin contact may occur.

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

• Non-impervious clothing which becomes contaminated with tetranitromethane should be removed promptly and any clothing which becomes wet with liquid tetranitromethane should be removed immediately and not reworn until the tetranitromethane 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 tetranitromethane contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to solid or liquid tetranitromethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

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

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

• Employees who handle solid or liquid tetranitromethane 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 tetranitromethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as an ingredient in manufacture of liquid explosives; use as an octane number improver in diesel fuels	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a laboratory analytical reagent as a nitrating agent; use in research 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 solid or liquid tetranitromethane or strong concentrations of tetranitromethane 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 promptly. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If solid or liquid tetranitromethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid tetranitromethane or 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 immediately.

• **Breathing**

If a person breathes in large amounts of tetranitromethane, 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 tetranitromethane 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 tetranitromethane 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. Avoid shock and friction if liquid spills on combustible matter such as wood and paper.

• Waste disposal method:

Liquid tetranitromethane may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill. Solid tetranitromethane may be collected in the most convenient manner and disposed of in a secured sanitary landfill. Care should be taken when disposing, since tetranitromethane is a weak explosive.

REFERENCES

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RESPIRATORY PROTECTION FOR TETRANITROMETHANE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Vapor Concentration	
5 ppm or less	Any chemical cartridge respirator with a full facepiece and a cartridge containing non-combustible sorbents and providing protection against tetranitromethane. A gas mask with a chin-style or a front- or back-mounted canister containing non-combustible sorbents and providing protection against tetranitromethane. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 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	A gas mask containing non-combustible sorbents and providing protection against tetranitromethane. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Tetryl

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: $(NO_2)_3C_6H_2N(NO_2)CH_3$
- Synonyms: 2,4,6-trinitrophenylmethylnitramine; N-methyl-N,2,4,6-tetranitroaniline; nitramine; tetralite
- Appearance and odor: Colorless to yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetryl is 1.5 milligrams of tetryl per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tetryl 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 tetryl may cause irritation of the eyes, nose, and throat. It may stain the skin and hair yellow. It may cause an allergic skin rash. Several days' exposure to high concentrations may cause headaches and nose bleeding. Occasionally, coughing and choking occur. Severe prolonged exposure may cause insomnia, nausea, vomiting, irritability, and anemia. In animals, it has caused liver and kidney damage, and severe breathing difficulties which may be delayed in onset.

- **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 tetryl.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tetryl 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 tetryl may be at increased risk from exposure. Examination of the respiratory tract, eyes, liver, central nervous system, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Tetryl has been shown to cause anemia in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Tetryl dust causes severe sensitization dermatitis and irritation of the upper respiratory tract. Dogs injected subcutaneously with fatal doses showed degeneration of renal tubules, liver necrosis, and occasional pulmonary edema. Dermatitis in workers appears as early as the first week of exposure to the dust with itching of the eyes; there is a progression to erythema and edema occurring most often on the nasal folds, cheeks, and neck; papules and vesicles may develop; the remainder of the body is rarely affected. The severest forms show massive generalized edema with partial obstruction of the trachea due to swelling of the tongue and require

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

hospitalization; exfoliation usually occurs after the edema subsides. The majority of these effects occur between the 10th and 20th days of exposure; upon cessation of exposure there is rapid abatement of the mild symptoms, and after 3 to 10 days disappearance of physical signs. Contact with tetryl causes a bright yellow staining, most often seen on the palms, face, neck, and in the hair. The irritant effects on the upper respiratory tract range from the nares to the bronchi and cause burning, itching, sneezing, coryza, epistaxis, and cough; the symptoms may begin the first day of exposure or as late as the third month; upon removal from exposure the symptoms regress over 2 to 4 weeks. Other effects reported in tetryl workers are irritability, easy fatigability, malaise, headache, lassitude, insomnia, nausea, and vomiting. Anemia, either of the marrow depression or deficiency type, has been observed among tetryl workers. Conjunctivitis may be caused by rubbing the eyes with contaminated hands or by airborne dust; keratitis and iridocyclitis have occurred.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 287
2. Boiling point (760 mm Hg): 187 C (369 F) (explodes)
3. Specific gravity (water = 1): 1.6– 1.7
4. Vapor density (air = 1 at boiling point of tetryl): Not applicable
5. Melting point: 129 C (264 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): 0.02
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat and shock
2. Incompatibilities: Contact of tetryl with some oxidizable materials may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving tetryl.
4. Special precautions: Protect from shock

- **Flammability**

1. Flash point: Explodes
2. Flammable limits in air, % by volume: Not applicable
3. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): 26 cm
4. Explosion temperature (temperature required to cause explosion in five seconds): 257 C (495 F)
5. Extinguishant: Water may be used on small fires. Do not attempt to extinguish large fires.

- **Warning properties**

Concerning the effects of tetryl on the eye, Grant states that "conjunctivitis may be caused by rubbing the eyes with contaminated hands, but more commonly airborne dust is responsible. Conjunctivitis is usually accompanied by dermatitis of the face, but may persist considerably longer than the skin rash. Keratitis and iridocyclitis are also said to have occurred in association with the conjunctivitis." No quantitative information is available concerning what concentrations in air produce the conjunctivitis, 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 tetryl on a cellulose membrane filter with subsequent extraction with N,N-diethylethanolamine and spectrophotometric analysis. An analytical method for tetryl 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 tetryl or liquids containing tetryl.

• If employees' clothing may have become contaminated with tetryl, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with tetryl should be removed promptly and not reworn until the tetryl is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where tetryl or liquids containing tetryl may contact the eyes.

SANITATION

• Workers subject to skin contact with tetryl should wash any areas of the body which may have contacted tetryl at the end of each work day.

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

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

• Employees who handle tetryl or liquids containing tetryl 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 tetryl may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of explosives for use in blasting caps, boosters in high explosive shells, aircraft cannons, shells, and as a primer for less sensitive explosives; use during the formulation of binary explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a pH indicator	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 tetryl or liquids containing tetryl 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 tetryl or liquids containing tetryl get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tetryl or liquids containing tetryl penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention promptly.

• **Breathing**

If a person breathes in large amounts of tetryl, 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 tetryl or liquids containing tetryl 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 tetryl is spilled, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill.
3. Attempt to reclaim spilled material; however, do not sweep or burn unless this is supervised by explosives experts.

• Waste disposal method:

Tetryl may be disposed of only by explosives experts.

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RESPIRATORY PROTECTION FOR TETRYL

Condition	Minimum Respiratory Protection* Required Above 1.5 mg/m³
Particulate Concentration	
7.5 mg/m³ or less	Any dust and mist respirator, except single-use.**
15 mg/m³ or less	Any dust and mist respirator, except single-use respirator or quarter mask.** Any fume respirator or high efficiency particulate filter respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
75 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.
1500 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
3000 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 3000 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.

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

Occupational Health Guideline for Soluble Thallium 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 thallium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

• Names and Formulas: 1) Thallium sulfate: Tl_2SO_4; 2) Thallium acetate: $TlC_2H_3O_2$; 3) Thallium nitrate: $TlNO_3$

• Appearance and odor: Thallium sulfate, thallium acetate, and thallium nitrate are all colorless, odorless solids.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble thallium compounds is 0.1 milligram of soluble thallium compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Soluble thallium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin, or if they are swallowed. They may enter the body thorugh the skin.

• **Effects of overexposure**

Soluble thallium compounds are very toxic and cause cumulative intoxication. Many deaths have resulted from swallowing these compounds. Poisoning from industrial exposure has been rarely reported — those that have, were not fatal. Swallowing soluble thallium compounds may cause nausea, vomiting, diarrhea, abdominal pain, and bleeding from the gut. These symptoms are followed or accompanied by drooping of the eyelids, crossed eyes, weakness, numbness, and tingling of the arms and legs, trembling, and pain and tightness of the chest. The hair may fall out after two to three weeks. Severe intoxication may result in prostration, rapid heartbeat, convulsions, and psychosis. Recovery may be complete but permanent effects such as staggering, visual difficulties, trembling, and mental abnormalities have been reported. Liver and kidney damage have occurred. Repeated exposure over a prolonged period may produce variable symptoms. These may include loss of hair, soreness of the mouth, trembling, severe weight loss, and emotional disturbance.

• **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 thallium compounds.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble thallium compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, nervous system, lungs, liver, kidneys, gastrointestinal tract, and body hair should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to thallium, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

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.

• **Summary of toxicology**

Soluble thallium compounds are extremely toxic and cause a cumulative intoxication affecting primarily the nervous system and the body hair. Many deaths have resulted from ingestion. The lethal oral dose of thallium acetate for humans is estimated to be about 12 mg/kg body weight. Ingestion causes nausea, vomiting, diarrhea, abdominal pain and gastrointestinal hemorrhage, which usually occur within 1 to 3 days. These are followed or accompanied by ptosis, strabismus; peripheral neuritis, pain, weakness, and paresthesias in the legs, tremor; retrosternal tightness and chest pain. Severe alopecia usually occurs after 2 to 3 weeks and is pathognomonic of the toxic effects of thallium. Severe intoxication may result in prostration, tachycardia, blood pressure fluctuations, convulsive seizures, choreaform movements, and psychosis. Recovery may be complete, but permanent residual effects such as ataxia, optic atrophy, tremor, mental abnormalities, and footdrop have been reported. In cases of fatal intoxication, typical autopsy findings include pulmonary edema, necrosis of the liver, nephritis, and degenerative changes in peripheral axons. Prolonged ingestion of thallium produces a variable clinical picture which includes stomatitis, tremor, cachexia, polyneuropathy, alopecia, and emotional disturbance. In a study of 15 workers who had handled solutions of organic thallium salts over a 7.5-year period, 6 workers suffered thallium intoxication; chief complaints were abdominal pain, fatigue, weight loss, pain in the legs, and nervous irritability; 3 of the workers had albuminuria and 1 had hematuria.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

These data correspond to the the three substances identified above.

1. Molecular weight: 1) 504.81; 2) 263.41; 3) 266.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1) 6.8; 2) 3.7; 3) 5.5
4. Vapor density (air = 1 at boiling point of soluble thallium compounds): Not applicable
5. Melting point: 1) 632 C (1170 F); 2) 110 C (230 F); 3) 206 C (403 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 1) 4.87; 2) Very soluble; 3) 10
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: Data not available
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Water, carbon dioxide, foam, dry chemical

• **Warning properties**

Grant describes some effects on the eye produced by systemic thallium poisoning. In addition, Grant states that "experiments concerned with the local effects of thallium on the eye suggest that contact of thallium salts with the eye, such as by accidental splash contamination, is unlikely to cause serious damage, especially if promptly washed away with water. Experimentally, a rather drastic exposure of a rabbit eye for ten minutes to a neutral saturated solution of thallium chloride, with the epithelium preliminarily removed to facilitate penetration, caused moderate edema and haze in the cornea, which gradually cleared from the periphery but left a nebulous area axially. Splash contact with intact epithelium presumably would be even less damaging."

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 filter with a subsequent atomic absorption spectrophotometric analysis. An analytical method for soluble thallium 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).

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 soluble thallium compounds where skin contact may occur.

• If employees' clothing may have become contaminated with soluble thallium compounds, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with soluble thallium compounds should be removed promptly and not reworn until the soluble thallium compounds are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where soluble thallium compounds may contact the eyes.

SANITATION

• Skin that becomes contaminated with soluble thallium compounds should be promptly washed or showered to remove any soluble thallium compounds.

• Eating and smoking should not be permitted in areas where soluble thallium compounds are handled, processed, or stored.

• Employees who handle soluble thallium compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in laboratory for analytical and research purposes	Local exhaust ventilation; personal protective equipment
Use in manufacture of special lenses, plates and prisms, medicinals, pyrotechnic products, and fuel additives for internal combustion engines	Local exhaust ventilation; personal protective equipment
Manufacture of soluble thallium compounds and application as a rodenticidal agent	Local exhaust ventilation; personal protective equipment; product 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 soluble thallium 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 this chemical.

• **Skin Exposure**

If soluble thallium compounds get on the skin, promptly flush the contaminated skin with water. If soluble thallium compounds penetrate through the clothing, remove the clothing promptly and flush the skin with water. Get medical attention.

• **Breathing**

If a person breathes in large amounts of soluble thallium 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 thallium 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 thallium compounds are 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 a sealed container for disposal. Large quantities may be reclaimed; however, if this is not practical, collect spilled material in the most convenient and safe manner and deposit in sealed containers for disposal.
3. Liquids containing soluble thallium compounds may be absorbed in vermiculite, dry sand, earth, or a similar material and deposited in sealed containers for disposal.

• Waste disposal method

Soluble thallium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOLUBLE THALLIUM COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Dust or Mist Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
1 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m³ or less	A powered air-purifying respirator with a full facepiece, helmet, or hood, and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	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 Thiram

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_{12}N_2S_4$
- Synonyms: Tetramethylthiuram disulfide
- Appearance: Colorless to cream solid (some commercial products are dyed blue).

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Thiram 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**

Thiram can cause irritation of the eyes, nose, throat, and skin. It may cause an allergic skin rash. Thiram is thought to have similar effects as antabuse which include nausea, vomiting, diarrhea, and loss of appetite. After ingestion of alcohol, individuals taking antabuse may experience skin redness, hives, itching, pulsating headache, flushing, sweating, nausea, vomiting, diarrhea, weakness, dizziness, and difficulty in breathing. Thiram has caused birth defects in offspring of animals given large doses of thiram by mouth.

- **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 thiram.

- **Recommended medical surveillance**

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

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

—Skin disease: Thiram is a skin sensitizer. 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**

Thiram (tetramethylthiuram disulfide) dust irritates the respiratory tract, eyes, and skin, and causes sensitization dermatitis. Thiram was teratogenic (skeletal malformations) in hamsters given a single oral dose of 250 mg/kg during the period of organogenesis and in mice given oral doses of 5 to 30 mg/animal daily between days 6 and 17 of pregnancy. In exposed humans, sensitization dermatitis in the form of eczema has occurred on the hands, forearms, and feet. Thiram is thought to have similar toxic effects to antabuse, which include nausea, vomiting, diarrhea, and loss of appetite. Ingestion of ethanol by persons taking antabuse has caused a severe reaction characterized by a rapid skin response of a nonallergic nature, flushing, erythema, pruritis, urticaria, headache, nausea, vomiting, diarrhea, weakness, dizziness, and difficult breathing.

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: 240
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 1.40
  4. Vapor density (air = 1 at boiling point of thiram): Not applicable
  5. Melting point: 140 C (284 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids or oxidizable materials may cause formation of toxic gases such as hydrogen sulfide.
  3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, carbon disulfide, and carbon monoxide) may be released in a fire involving thiram.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 89 C (192 F) (closed cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Carbon dioxide, foam, dry chemical
- **Warning properties**

Warning properties are not considered since the vapor pressure is negligible.

Grant states that "as a dust or spray it is irritating to the eyes . . . ." No quantitative information is available concerning the eye irritation threshold, 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 thiram on a membrane filter with subsequent chemical treatment and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure thiram may be used. An analytical method for thiram 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 thiram or liquids containing thiram, where skin contact may occur.
- If employees' clothing may have become contaminated with solid thiram, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with thiram should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of thiram from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the thiram, the person performing the operation should be informed of thiram's hazardous properties.
- Non-impervious clothing which becomes contaminated with thiram should be removed promptly and not reworn until the thiram is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where thiram or liquids containing thiram may contact the eyes.

SANITATION

- Skin that becomes contaminated with thiram should be promptly washed or showered with soap or mild detergent and water to remove any thiram.
- Eating and smoking should not be permitted in areas where thiram is handled, processed, or stored.

• Employees who handle thiram or liquids containing thiram 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 thiram may occur and control methods which may be effective in each case:

Operation	Controls
Use in rubber industry as an accelerator, peptizing agent, and vulcanizing agent	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during application as an agricultural fungicide as foliage spray for plants and trees, fruits and seeds	Handle mechanically; personal protective equipment
Use as a bacteriostat in commercial and surgical soap, antiseptics, sunburn oils and fats	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use as an animal repellant on plants or trees	Handle mechanically; 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 thiram or liquids containing thiram 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 thiram or liquids containing thiram get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If thiram or liquids containing thiram 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.

• **Swallowing**

When thiram or liquids containing thiram 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 thiram 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:

Thiram may be disposed of:

1. By making packages of thiram in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving thiram 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 THIRAM

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus. Any pesticide chemical cartridge respirator.
250 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. Any pesticide chin-style cartridge respirator with a full facepiece. A chin-style or a front- or back-mounted pesticide gas mask.
1500 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. A powered air-purifying pesticide respirator with a full facepiece, helmet, or hood.
Greater than 1500 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 Inorganic Tin Compounds (as Tin)

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 inorganic tin compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Tin

- Formula: Sn
- Synonyms: Tin, metallic
- Appearance and odor: Odorless, dull silvery metal.

Stannous chloride

- Formula: $SnCl_2$
- Synonyms: Tin(II) chloride; tin dichloride
- Appearance and odor: Odorless, colorless to brown solid.

Stannic chloride

- Formula: $SnCl_4$
- Synonyms: Tin(IV) chloride; tin tetrachloride
- Appearance and odor: Colorless to yellow fuming liquid with an acrid odor.

Stannous sulfate

- Formula: $SnSO_4$
- Synonyms: Tin(II) sulfate
- Appearance and odor: Odorless, colorless to brown solid.

Potassium stannate

- Formula: $K_2SnO_3 3H_2O$
- Synonyms: Potassium stannate trihydrate
- Appearance and odor: Odorless, colorless to brown solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for inorganic tin compounds (as tin) is 2 milligrams of inorganic tin compounds (as tin) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tin, stannous chloride, stannic chloride, stannous sulfate, or potassium stannate can affect the body if they are inhaled or if they come in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: In general, the toxicity of inorganic tin salts is low. These compounds may cause irritation of the eyes, nose, throat, 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 inorganic tin compounds.

- **Recommended medical surveillance**

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

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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

—Skin disease: Certain inorganic tin compounds other than oxides are primary skin irritants. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

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

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

• **Summary of toxicology**

Inorganic tin compounds (except the oxides) irritate the eyes and skin. Subcutaneous injection of animals with sodium stannous tartrate at a daily dose of 12.5 mg/kg was fatal; death was preceeded by vomiting, diarrhea, and paralysis with twitching of the limbs. Daily administration to a dog of stannous chloride in milk at a level of 500 mg/kg produced paralysis after 14 months. Some inorganic tin compounds can cause skin or eye irritation because of acid or alkaline reaction produced with water; tin tetrachloride, stannous chloride, and stannous sulfate are strong acids; sodium and potassium stannate are strong alkalis.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Tin**

1. Molecular weight: 118.7
2. Boiling point (760 mm Hg): 2689 C (4873 F)
3. Specific gravity (water = 1): 5.8 to 7.3
4. Vapor density (air = 1 at boiling point of tin): Not applicable
5. Melting point: 232 C (450 F)
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

• **Physical data—Stannous chloride**

1. Molecular weight: 189.6
2. Boiling point (760 mm Hg): 605 C (1121 F)
3. Specific gravity (water = 1): 3.95
4. Vapor density (air = 1 at boiling point of stannous chloride): Not applicable
5. Melting point: 247 C (477 F)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 90
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Stannic chloride**

1. Molecular weight: 260.5
2. Boiling point (760 mm Hg): 114 C (237 F)
3. Specific gravity (water = 1): 2.23
4. Vapor density (air = 1 at boiling point of stannic chloride): 9
5. Melting point: −33 C (−27 F)
6. Vapor pressure at 20 C (68 F): 18 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Stannous sulfate**

1. Molecular weight: 214.8
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available (greater than 1)
4. Vapor density (air = 1 at boiling point of stannous sulfate): Not applicable
5. Melting point: 300 C (572 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 33
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Potassium stannate**

1. Molecular weight: 298.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.2
4. Vapor density (air = 1 at boiling point of potassium stannate): Not applicable
5. Melting point: 140 C (284 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 110
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: If moisture enters containers of stannic chloride, pressure may burst containers. At temperatures above 360 C (680 F), stannous sulfate decomposes to form toxic sulfur dioxide.

2. Incompatibilities: Contact of metallic tin with chlorine may cause adjacent combustible material to ignite. Contact of metallic tin with turpentine may cause fires and explosions. Contact of stannic chloride with water, alcohols, and amines may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving the tin chlorides and stannous sulfate.

4. Special precautions: Stannic chloride will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Not applicable
2. Minimum ignition temperature: a) Tin: 630 C (1166 F) (cloud); 430 C (806 F) (layer); For the other compounds: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For tin, water; for the other compounds, not applicable.

• **Warning properties**

According to Grant, tin tetrachloride (stannic chloride) is "highly irritating to the eyes and mucous membranes.

The irritation presumably is attributable to the hydrochloric acid which is generated when stannic chloride reacts with water." The threshold of eye irritation is not given.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by treatment with nitric and sulfuric acids, solution in hydrochloric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for inorganic tin 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 any possibility of skin contact with liquid stannic chloride.

• 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 stannous sulfate, potassium stannate, or liquids containing these compounds, where skin contact may occur.

• 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 stannous chloride or liquids containing stannous chloride.

• If employees' clothing may have become contaminated with solid stannous chloride, stannous sulfate, or potassium stannate, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with stannous chloride, stannic chloride, stannous sulfate, or potassium stannate 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 liquid stannic chloride, 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 stannous sulfate, potassium stannate, or liquids containing these compoumay 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 stannic chloride, stannous sulfate, or potassium stannate should be removed immediately and not reworn until the contaminant is removed from the clothing.

• Non-impervious clothing which becomes wet with stannous chloride should be removed promptly and not reworn until the stannous chloride 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 liquid stannic chloride, stannous sulfate or liquids containing stannous sulfate, or potassium stannate or liquids containing potassium stannate contacting the eyes.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where stannous chloride or liquids containing stannous chloride may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid stannic chloride, stannous sulfate or liquids containing stannous sulfate, or potassium stannate or liquids containing potassium stannate,

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

SANITATION

- Skin that becomes contaminated with stannic chloride, stannous sulfate, or potassium stannate should be immediately washed or showered to remove any contaminant.
- Skin that becomes wet with stannous chloride should be promptly washed or showered to remove any stannous chloride.
- Employees who handle stannous chloride, stannic chloride, stannous sulfate, or potassium stannate 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 inorganic tin compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, roasting, and smelting of cassiterite ore; during foundry operations and finishing operations	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of stannic chloride in dyeing silk; manufacture of blueprint paper; as a perfume stabilizer in soap; in the preparation of lubricating oil additives; in treating glass surfaces; as a catalyst in manufacture of pharmaceuticals; and as a bleaching agent for sugar	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of stannous chloride in acidic electrotinning baths; manufacture of blueprint paper; as an antisludge agent in lubricating oils; as a perfume stabilizer in soap; as a catalyst in organic reactions; as an additive in drilling mud; in silvering of mirrors; and as a food additive	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in production of stannous fluoride or stannous pyrophosphate for use tinning baths and for formulations for remineralization of teeth; use of stannous fluorborate in commercial tin-plating baths; use in production of sodium stannate	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in production of potassium stannate; use of stannous perchlorate in tin-plating solutions; use of stannic chromate as a ceramic pigment	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of tin hydride to gas-phase plate tin on metal and ceramic surfaces; use of stannous sulfide as a pigment, as a catalyst, and in manufacture of bearing materials	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in production of stannous sulfate for use in acidic electrotinning baths and in dyeing textiles	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of stannous oleate or stannous 2-ethyl hexoate as a catalyst for urethane and other polymer foams and as a fabric water-repellant	Personal protective equipment
Use of stannous acetate as a catalyst and agent to promote exhaustion of dyes	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use of heavy metal stannates as additives to ceramic dielectric materials	Process enclosure; local exhaust ventilation; personal protective equipment
Use of stannous tartrate in printing and dyeing of textiles	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

Use of stannous oxalate as a catalyst in esterification reactions and in coal hydrogenation; use of stannic bromide for metallurgical separation of minerals in the laboratory	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 tin, stannous sulfate, or potassium stannate 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 inorganic tin compounds get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If inorganic tin compounds 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 inorganic tin 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 inorganic tin 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, 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 tin, stannous chloride, stannic chloride, stannous sulfate, or potassium stannate are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled or leaked material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing inorganic tin compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Inorganic tin compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR INORGANIC TIN COMPOUNDS (AS TIN)

Condition	Minimum Respiratory Protection* Required Above 2 mg/m³
Particulate Concentration	
10 mg/m³ or less	Any dust and mist respirator, except single-use.**
20 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume or high efficiency particulate filter respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
100 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.
400 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 400 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus with a full facepiece.

*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 Organic Tin Compounds (as Tin)

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 organic tin compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Dibutyltin di-2-ethylhexoate

- Formula: $(C_4H_9)_2Sn(C_8H_{15}O_2)_2$
- Synonyms: Dibutyltin dioctoate
- Appearance and odor: Waxy solid with a weak odor.

Bis(tri-n-butyltin) oxide

- Formula: $((C_4H_9)_3Sn)_2O$
- Synonyms: TBTO
- Appearance and odor: Colorless to yellow liquid with a weak odor.

Triphenyltin chloride

- Formula: $(C_6H_5)_3SnCl$
- Synonyms: None
- Appearance and odor: Colorless to yellow solid with a characteristic odor.

Dibutyltin dichloride

- Formula: $(C_4H_9)_2SnCl_2$
- Synonyms: None
- Appearance: Light tan or colorless solid or semi-solid.

Dibutyltin diacetate

- Formula: $(C_4H_9)_2Sn(C_2H_3O_2)_2$
- Synonyms: None
- Appearance and odor: Colorless liquid with a weak vinegar odor.

Tetrabutyltin

- Formula: $(C_4H_9)_4Sn$
- Synonyms: Tetra-n-butyltin
- Appearance and odor: Colorless liquid with a distinct, characteristic odor.

Stannous 2-ethylhexoate

- Formula: $Sn(C_8H_{15}O_2)_2$
- Synonyms: Stannous octoate; tin octoate
- Appearance and odor: Pale yellow, viscous liquid with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for organic tin compounds is 0.1 milligram of organic tin compounds (as tin) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 0.1 milligram of tin per cubic meter of air averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Organotin Compounds should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Organic tin compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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

They can also affect the body if they are swallowed and they may be absorbed through the skin.

• **Effects of overexposure**

Little is known of the toxicity of monoalkyl tin compounds except that the toxicity of monoethyl tin chloride is low. Dialkyl tin compounds have caused irritation of the skin and damage to the liver and bile ducts in animals. This has resulted in animal deaths from liver failure and peritonitis. Swallowing diethyl tin has caused permanent damage to the nervous system and deaths in humans. Trialkyl and tetraalkyl tin compounds have caused nervous system damage in animals. Trialkyl and dibutyl tins have caused skin burns in humans. Tetramethyl and tetraethyl tin have caused headache and vomiting in humans. Tributyl tin compounds have caused severe skin burns 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 organic tin compounds.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to organic tin compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, eyes, liver, and urinary tract should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since some organic tin compounds may cause urinary retention, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Organic tin compounds cause hepatic necrosis in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—A complete blood count: Organic tin compounds cause hemolysis in animals. A complete blood count should be performed including a red cell count, a white cell count, a differential on a stained smear, as well as hemoglobin and hematocrit.

—Eye disease: Since some organic tin compounds may produce neurological damage, the eyes should be examined for such abnormalities as glaucoma and choked disc; general tests of visual acuity should be performed as well. In addition, evidence indicating past or present increased intracranial pressure should be evaluated.

—Cardiovascular system: An electrocardiogram should be performed on workers over 40 years of age and where indicated.

—Skin disease: Organic tin 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**

The organic tin compounds, chiefly solids and liquids, cause irritation of the eyes, throat, and skin; some produce cerebral edema, while others cause hepatic necrosis. Oral administration of a preparation of organic tin containing diethyltin di-iodide and up to 10% triethyltin for treatment of human furunculosis resulted in 217 cases of poisoning, 100 of which were fatal. After a latent period of 4 days there was severe persistent headache followed by vertigo, visual disturbances including photophobia, abdominal pain, vomiting, and urinary retention; the more severe cases showed transient or permanent paralysis and psychic disturbances. Residual symptoms in those who recovered included persistent headache, diminished visual acuity, partial paresis, focal anesthesia, and in four severe cases, flaccid paraplegia with incontinence. The most significant lesion found at necropsy was cerebral edema. Repeated oral administration to rats of 50 mg/kg of dibutyltin chloride resulted in inflammation of bile ducts and hepatic necrosis; repeated skin applications of 10 mg/kg caused severe local skin injury and bile duct damage. Triethyltin sulfate administered repeatedly to rats at 10 mg/kg caused tremors and paresis, which in some animals progressed to complete paralysis and death; it was equally toxic by mouth and by injection. In mice, tributyltin chloride had a marked hemolytic action, while dibutyl and tetrabutyl tin were less markedly hemolytic. Workers exposed to the vapor or fume of butyltin compounds developed sore throat and cough several hours after exposure. Chemical burns from organic tin compounds may result from only brief contact with the skin; pain is usually moderate and itching is the chief symptom; healing is usually complete within 7 to 10 days. When a worker was splashed in the face with a tributyltin compound, lacrimation and severe conjunctivitis appeared within minutes, despite immediate lavage, and persisted for 4 days; at the end of 7 days the eyes appeared normal.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Dibutyltin di-2-ethylhexoate**

1. Molecular weight: 522.7
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.07
4. Vapor density (air = 1 at boiling point of dibutyltin di-2-ethylhexoate): Not applicable
5. Melting point: 54 C (129 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Bis(tri-n-butyltin) oxide**

1. Molecular weight: 595.4

2. Boiling point (760 mm Hg): 254 C (489 F) at 50 mm Hg
3. Specific gravity (water = 1): 1.17
4. Vapor density (air = 1 at boiling point of bis(tri-n-butyltin)oxide): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Much less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 20 ppm
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Triphenyltin chloride**

1. Molecular weight: 385.5
2. Boiling point (760 mm Hg): 240 C (464 F) at 13 mm Hg
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of triphenyltin chloride): Not applicable
5. Melting point: 106 C (223 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Dibutyltin dichloride**

1. Molecular weight: 303.8
2. Boiling point (760 mm Hg): 135 C (275 F) at 10 mm Hg
3. Specific gravity (water = 1): 1.36
4. Vapor density (air = 1 at boiling point of dibutyltin dichloride): Not applicable
5. Melting point: 43 C (109 F)
6. Vapor pressure at 20 C (68 F): 2 mm Hg/100 C (212 F)
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Dibutltin diacetate**

1. Molecular weight: 351
2. Boiling point (760 mm Hg): 144 C (291 F) at 10 mm Hg
3. Specific gravity (water = 1): 1.32
4. Vapor density (air = 1 at boiling point of dibutyltin diacetate): Not applicable
5. Melting point: 10 C (50 F)
6. Vapor pressure at 20 C (68 F): 1.3 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Tetrabutyltin**

1. Molecular weight: 347.2
2. Boiling point (760 mm Hg): 145 C (293 F) at 10 mm Hg
3. Specific gravity (water = 1): 1.06
4. Vapor density (air = 1 at boiling point of tetrabutyltin): Not applicable
5. Melting point: Less than −70 C (less than −94 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): Not applicable

• **Physical data—Stannous 2-ethylhexoate**

1. Molecular weight: 404.7
2. Boiling point (760 mm Hg): Decomposes at 200 C (392 F)
3. Specific gravity (water = 1): 1.26
4. Vapor density (air = 1 at boiling point of stannous 2-ethylhexoate): Not applicable
5. Melting point: Less than −25 C (less than −13 F)
6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving organic tin compounds.
4. Special precautions: Organic tin compounds will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: a) Dibutyltin di-2-ethylhexoate: Data not available; b) Bis(tri-n-butyltin) oxide: Greater than 100 C (212 F); c) Triphenyltin chloride: Data not available; d) Dibutyltin dichloride: 168 C (334 F); e) Dibutyltin diacetate: 143 C (289 F); f) Tetrabutyltin: 124 C (255 F); g) Stannous 2-ethylhexoate: 142 C (287 F)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available (probably because too high boiling points)
4. Extinguishant: Water, foam, dry chemical, and carbon dioxide

• **Warning properties**

Concerning the toxicity of organic tin, Browning states "The eyes are rarely involved, but accidental splashing can cause lacrimation and intense suffusion of the conjunctiva which persists for several days, but with no permanent injury."

Grant lists several toxic effects produced by triethyltin on the eye, but these injuries are caused by systemic poisoning, not by a local effect on the eye.

The NIOSH Criteria Document cites Landa et al. as having observed eye and upper respiratory tract irritation from bis(tributyltin) oxide at an average air concentration of 0.05 mg/m^3 measured as tin, but noted that this concentration may not be entirely accurate since the limit of sensitivity of the measurement method used was 0.1 mg/m^3.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of organic tin compounds on a filter, followed by chemical treatment and subsequent spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure organic tin compounds may be used. An analytical method for organic tin compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with triphenyltin chloride or liquids containing triphenyltin chloride.

• 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 dibutyltin di-2-ethylhexoate or liquids containing dibutyltin di-2-ethylhexoate, liquid bis(tri-n-butyltin) oxide, solid or liquid dibutyltin diacetate, liquid tetrabutyltin, or liquid stannous 2-ethylhexoate.

• 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 dibutyltin dichloride or liquids containing dibutyltin dichloride, where skin contact may occur.

• If employees' clothing has had any possibility of being contaminated with solid triphenyltin chloride or dibutyltin dichloride, employees should change into uncontaminated clothing before leaving the work premises.

• If employees' clothing may have become contaminated with solid dibutyltin di-2-ethylhexoate, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate 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 triphenyltin chloride or liquids containing triphenyltin chloride, 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 dibutyltin dichloride or liquids containing dibutyltin dichloride 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 triphenyltin chloride or dibutyltin dichloride should be removed immediately and not reworn until the contaminant is removed from the clothing.

• Non-impervious clothing which becomes contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide,dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate 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 triphenyltin chloride or liquids containing triphenyltin chloride contacting the eyes.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where dibutyltin di-2-ethylhexoate or liquids containing dibutyltin di-2-ethylhexoate, dibutyltin dichloride or liquids contain-

ing dibutyltin dichloride, liquid bis(tri-n-butyltin) oxide, solid or liquid dibutyltin diacetate, liquid tetrabutyltin, or liquid stannous 2-ethylhexoate may contact the eyes.

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

SANITATION

• Skin that becomes contaminated with triphenyltin chloride or dibutyltin dichloride should be immediately flushed with large amounts of water to remove any contaminant.

• Workers subject to skin contact with solid dibutyltin di-2-ethylhexoate, triphenyltin chloride, or dibutyltin dichloride should wash with soap or mild detergent and water any areas of the body which may have contacted any contaminant at the end of each work day.

• Skin that becomes contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.

• Eating and smoking should not be permitted in areas where dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, dibutyltin dichloride, dibutyltin diacetate, or tetrabutyltin are handled, processed, or stored.

• Employees who handle dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate 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 organic tin compounds may occur and control methods which may be effective in each case:

Operation	Controls
Use as a stabilizing agent against degradation effects fo light, heat, and oxygen on poly vinyl chloride, neoprene, chlorinated polyethylenes, vinyl copolymers, silicones, and polyamides	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst in organic and inorganic synthesis in condensation, esterification, halogenation, hydrogenation, oxidation, and polymerization	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of insecticides, bactericides, fungicides, and molluscides; use as U.S. Food and Drug-sanctioned chemical on agricultural crops	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of rodent repellants for wire cable	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as veterinary medicine as poultry anthelmintic	General dilution ventilation
Use as a fuel additive and lubricant	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 organic tin 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 dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate get on the skin, immediately flush with large amounts of water, then wash with soap or mild detergent and water. If dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate soak through the clothing, remove the clothing immediately and flush with large amounts of water and then wash using soap or mild detergent and water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of organic tin compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respi-

ration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When organic tin 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, 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 organic tin compounds are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing organic tin compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Organic tin compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR ORGANIC TIN COMPOUNDS (AS TIN)

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
1 mg/m³ or less	A chemical cartridge respirator with an organic vapor cartridge(s) and a dust and mist filter. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m³ or less	Any chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and high efficiency filter (s). 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 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	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 Titanium 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: TiO_2
- Synonyms: Rutile; anatase; brookite
- Appearance and odor: White powder with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for titanium dioxide is 15 milligrams of titanium dioxide (total dust) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for titanium dioxide a Threshold Limit Value of 10 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Titanium dioxide can affect the body if it is inhaled.

- **Effects of overexposure**

Slight change in the lungs 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 titanium dioxide.

- **Recommended medical surveillance**

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

—Chronic respiratory disease: Titanium dioxide is a nuisance dust. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of titanium dioxide 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**

Titanium dioxide dust is a mild pulmonary irritant. Rats repeatedly exposed to concentrations of 10 to 328 million particles per cubic foot of air for as long as 13 months showed small focal areas of emphysema, which were attributed to large deposits of dust; there was no evidence of any specific lesion being produced by titanium dioxide. Three of 15 workers who had been exposed to titanium dioxide dust showed radiographic signs in the lungs resembling "slight fibrosis," but disabling injury did not occur; the magnitude and duration of exposure were not specified. In the lungs of three workers involved in processing titanium dioxide pigments, deposits of the dust in the pulmonary interstitium were associated with cell destruction and slight fibrosis; the findings indicated that titanium dioxide is a mild pulmonary irritant.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 79.9
2. Boiling point (760 mm Hg): Less than 3000 C (less than 5432 F)
3. Specific gravity (water = 1): 3.9 – 4.2
4. Vapor density (air = 1 at boiling point of titanium dioxide): Not applicable
5. Melting point: 1640 C (2984 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

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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- **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**

According to Grant, titanium dioxide "is a white pigment which is insoluble in water and very inert. It has been introduced by tattooing into the corneas of rabbits and patients having corneal scars, and has caused permanent white coloration but no irritation." For the purposes of this guideline, therefore, titanium dioxide is not treated as 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 titanium dioxide on a filter, followed by treatment with nitric acid, solution by heating with sulfuric acid and ammonium sulfate, and atomic desorption spectrophotometric analysis. An analytical method for titanium dioxide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during mining, purification, packaging, and distribution	General dilution ventilation; personal protective equipment
Use as a pigment in manufacture of paints, varnishes, and lacquers to impart whiteness, opacity, and brightness	General dilution ventilation; personal protective equipment
Use in manufacture of paper used in coatings and fillers to improve opacity and brightness; manufacture of paper, photographic papers, paper packaging, and cellophane coatings	General dilution ventilation; personal protective equipment
Use as a white pigment in manufacture of plastics; blow-molded plastic containers	General dilution ventilation; personal protective equipment
Use in manufacture of elastomers for use in tire sidewalls, footwear, floor mats, gloves, rainwear, and wall coverings; use in manufacture of floor coverings	General dilution ventilation; personal protective equipment
Use in manufacture of ceramics and glass for capacitors, electromechanical transducers, welding-rod coatings, and glass fibers	General dilution ventilation; personal protective equipment
Use in manufacture of printing inks for flexographic, gravure, and letter press inks; packaging, publication, offset, and screen processing inks	General dilution ventilation; personal protective equipment

Use in manufacture of coated fabrics and textiles on natural/ artificial leather, oilcloth, upholstery materials, and wall coverings; as a delustrant for acrylic, nylon, and spandex fibers	General dilution ventilation; personal protective equipment
Use in manufacture of building materials in roofing granules, ceiling tiles, cement-curing aids, and titanium carbide cutting tools	General dilution ventilation; personal protective equipment
Use in manufacture of cosmetics, food color additives, and synthetic diamonds	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 titanium dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

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

• If titanium dioxide 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 titanium dioxide should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Titanium dioxide may be disposed of in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR TITANIUM DIOXIDE

Condition	Minimum Respiratory Protection* Required Above 15 mg/m³
Dust or Mist Concentration	
75 mg/m³ or less	Any dust and mist respirator.
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 7,5000 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.

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

Occupational Health Guideline for Toluene

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: $C_6H_5CH_3$
- Synonyms: Toluol; phenylmethane; methylbenzene
- Appearance and odor: Colorless liquid with an aromatic odor, like benzene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for toluene is 200 parts of toluene per million parts of air (ppm) averaged over an eight-hour work shift, and during any such work shift, 300 ppm toluene may not be exceeded except that a peak of 500 ppm toluene is permitted for 10 minutes during the eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 100 ppm toluene averaged over an eight-hour work shift with a ceiling level of 200 ppm averaged over a ten-minute period. The NIOSH Criteria Document for Toluene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Toluene 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: Toluene may cause irritation of the eyes, respiratory tract, and skin. It may also cause fatigue, weakness, confusion, headache, dizziness, and drowsiness. Peculiar skin sensation may be produced such as a "pins and needles feeling" or numbness. Very high concentrations may cause unconsciousness and death. The liquid splashed in the eye may cause irritation and temporary damage. Inhalation may also cause difficulty in seeing in bright light. If liquid toluene is splashed in the eyes, it will cause temporary irritation.

2. Long-term Exposure: Repeated or prolonged exposure to liquid toluene may cause drying and cracking 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 toluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to toluene 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. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since proper kidney function is necessary for biologic monitoring, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be analyzed for hippuric acid to obtain a background level.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Hippuric acid level in urine may be an indicator of the level of toluene exposure.

- **Summary of toxicology**

Toluene vapor causes narcosis. Controlled exposure of human subjects to 200 ppm for 8 hours produced mild fatigue, weakness, confusion, lacrimation, and paresthesia; at 600 ppm for 8 hours there were also euphoria, headache, dizziness, dilated pupils and nausea; at 800

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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ppm for 8 hours, symptoms were more pronounced, and after-effects included nervousness, muscular fatigue, and insomnia persisting for several days. Severe but reversible liver and kidney injury occurred in a person who was a glue-sniffer for 3 years; the chief component of the inhaled solvent was toluene (80% V/V); other ingredients were not listed. In workers exposed for many years to concentrations in the range of 80 to 300 ppm, there was no clinical or laboratory evidence of altered liver function. Toluene exposure does not result in the hematopoietic effects caused by benzene; the myelotoxic effects previously attributed to toluene are judged by more recent investigations to be the result of concurrent exposure to benzene present as a contaminant in the commercial toluene used. Most of the toluene absorbed from inhalation is metabolized to benzoic acid, conjugated with glycine in the liver to form hippuric acid, and excreted in the urine; the average amount of hippuric acid excreted in the urine by individuals not exposed to toluene is approximately 0.7 to 1.0 g/l of urine. The liquid splashed in the eyes of two workers caused transient corneal damage and conjunctival irritation; complete recovery occurred within 48 hours. Repeated or prolonged skin contact with liquid toluene has a defatting action, causing drying, fissuring, and dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 92.1
  2. Boiling point (760 mm Hg): 111 C (231 F)
  3. Specific gravity (water = 1): 0.86
  4. Vapor density (air = 1 at boiling point of toluene): 3.14
  5. Melting point: −95 C (−139 F)
  6. Vapor pressure at 20 C (68 F): 22 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.05
  8. Evaporation rate (butyl acetate = 1): 2.24
- **Reactivity**
  1. Conditions contributing to instability: Containers may burst at elevated temperatures.
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon dioxide and carbon monoxide) may be released in a fire involving toluene.
  4. Special precautions: Toluene will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 4 C (40 F) (closed cup)
  2. Autoignition temperature: 480 C (896 F)
  3. Flammable limits in air, % by volume: Lower: 1.27; Upper: 7.1
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: The American National Standards Institute (ANSI) states that "the odor of toluene is detectable by most people at concentrations in the range of 10 to 15 ppm. The odor has little value as a warning property."

  Patty points out that olfactory fatigue occurs rapidly upon exposure to toluene.

  2. Eye Irritation Level: Grant states that "the vapors of toluene cause noticeable sensation of irritation to human eyes at 300 to 400 ppm in air, but even at 800 ppm irritation is slight."

  ANSI reports that "irritation of eyes, mucous membranes, and upper respiratory tract may occur while workers are exposed to low concentrations of toluene. There is a considerable range of variation (100 to 500 ppm) between individuals, some finding any concentration of toluene objectionable. Commercial grades of toluene vary in irritant properties."

  3. Evaluation of Warning Properties: Because of its irritant effects, toluene is judged to have 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 toluene. 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.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of toluene. 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 vapors using an adsorption tube with a subsequent desorption of toluene 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 toluene may be used. An analytical method for toluene 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).

Methods for Set V" (order number PB 262 524).

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 toluene.

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

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

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

• Where there is any possibility that employees' eyes may be exposed to toluene, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes wet with liquid toluene should be promptly washed or showered with soap or mild detergent and water to remove any toluene.

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

Operation	Controls
Use as a solvent in pharmaceutical, chemical, rubber, and plastics industries; as a thinner for paints, lacquer, coatings, and dyes; as a paint remover; insecticides	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as starting material and intermediate in organic chemical and chemical synthesis industries	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of artificial leather; fabric and paper coatings; photogravure ink production; spray surface coating; as a diluent (cellulose ester lacquers)	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as constituent in formulation of automotive and aviation fuels	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 liquid toluene 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 toluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and

water. If liquid toluene 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 toluene, 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 toluene has been swallowed, get medical attention immediately. Do not attempt to make the exposed 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 toluene 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. Toluene 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 toluene vapors are permitted.

• Waste disposal method:

Toluene may be disposed of by atomizing in a suitable combustion chamber.

ADDITIONAL INFORMATION

To find additional information on toluene, look up toluene in the following documents:

• Medical Surveillance for Chemical Hazards
• Respiratory Protection for Chemical Hazards
• Personal Protection and Sanitation for Chemical Hazards
• NIOSH Criteria Document for Toluene (July 1973)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR TOLUENE

Condition	Minimum Respiratory Protection* Required Above 200 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).
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

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

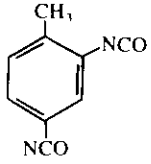
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TOLUENE DIISOCYANATE

INTRODUCTION

This guideline summarizes pertinent information about toluene diisocyanate (TDI) 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:** $C_9H_6N_2O_2$
- **Structure:**



- **Synonyms:** 2,4-Diisocyanato-1-methyl benzene; TDI; toluene-2, 4-diisocyanate; 2,4-toluene diisocyanate
- **Identifiers:** CAS 584-84-9; RTECS CZ6300000; DOT 2078, label required: "Poison"
- **Appearance and odor:** Colorless to pale yellow liquid with a sharp, pungent odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 174.16
2. Boiling point (at 760 mmHg): 251°C (484°F)
3. Specific gravity (water = 1): 1.22
4. Vapor density (air = 1 at boiling point of TDI): 6.0
5. Melting point: 21°C (69.8°F)
6. Vapor pressure at 25°C (77°F): 0.05 mmHg
7. Insoluble in water (reacts exothermically)
8. Evaporation rate (butyl acetate = 1): Much less than 1
9. Saturation concentration in air (approximate) at 25°C (77°F): 0.00657% (65.7 ppm)

- **Reactivity**

1. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with water, acids, bases, and amines may cause reactions that liberate heat and cause violent foaming and spattering.
2. Hazardous decomposition products: Toxic gases and vapors (e.g., oxides of nitrogen and carbon monoxide) may be released in a fire involving TDI.
3. Caution: TDI will attack some forms of plastic, rubber, and coatings.

- **Flammability**

1. Flash point: 132°C (270°F) (open cup)
2. Flammable limits in air, % by volume: Lower, 0.9; upper, 9.5
3. Extinguishant: Carbon dioxide, dry chemical powder, or foam
4. Class IIIB Combustible Liquid (29 CFR 1910.106), Flammability Rating 1 (NFPA)

- **Warning properties**

1. Odor threshold: 0.17 ppm
2. Eye irritation levels: 0.05-0.1 ppm
3. Evaluation of warning properties for respirator selection: Because of the lack of odor and irritant effects at concentrations below the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), TDI can only be detected above the NIOSH REL; thus TDI is treated as a chemical with poor warning properties.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for TDI is 0.02 parts of TDI per million parts of air (ppm) [0.14 milligrams of TDI per cubic meter of air (mg/m³)] as a ceiling concentration which shall at no time be exceeded. The NIOSH REL is 0.005 ppm (0.135 mg/m³) as a time-weighted average (TWA) concentration for up to a 10-hour workshift, 40-hour workweek, and the ceiling concentration is 0.02 ppm (0.14 mg/m³) as determined in any 10-minute sampling period. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 0.005 ppm (0.04 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek, and the short-term exposure limit (STEL) is 0.02 ppm (0.15 mg/m³) (Table 1).

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

Table 1.—Occupational exposure limits for toluene diisocyanate

	Exposure limits	
	ppm	mg/m³
OSHA PEL ceiling	0.02	0.14
NIOSH REL TWA	0.005	0.035
Ceiling (10 min)	0.02	0.14
ACGIH TLV® TWA	0.005	0.04
STEL	0.02	0.15

HEALTH HAZARD INFORMATION

• Routes of exposure

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

• Summary of toxicology

1. *Effects on animals:* Chronic administration of TDI by gavage to rats and mice produced cancer of the skin, pancreas, liver, mammary glands, and blood vessels. Chronic inhalation of TDI by rats caused increased fibrous tissue in the lung bronchioles, inflammation of the lungs and trachea, and death due to hemorrhage in the lungs. NIOSH will continue to monitor the research regarding TDI to determine whether the collective evidence justifies controlling this chemical as an occupational carcinogen.

2. *Effects on humans:* Exposure to TDI has caused severe bronchospasm, lung inflammation, fluid in the lungs, and decreased breathing capacity. It has also caused sensitization of the respiratory tract, as manifested by acute asthmatic reaction upon return to work after a period of time away from exposure.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to TDI can cause coughing, tightness of the chest, chest pain, nausea, vomiting, abdominal pain, headache, and insomnia. TDI can also cause severe skin irritation with redness, swelling, and blistering, and eye irritation with permanent damage if untreated.

2. *Long-term (chronic):* Exposure to TDI can cause respiratory sensitization; initial symptoms include coughing during the night, with difficult or labored breathing. 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 TDI, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system, eyes, and skin. 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 TDI at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindications to job placement, include a history of asthma or significant breathing impairment due to 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. The physician should note that a bronchial challenge test for nonspecific airway hyperreactivity (e.g., to cold air, exercise, methacholine, or histamine) may not be sufficiently sensitive or specific for identifying workers who are susceptible or sensitized to the effects of TDI.

• 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 TDI. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the physiologic function of the respiratory system, eyes, and skin as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires, pre- and post-shift tests of lung function, and chest X-rays. At the current state of knowledge, tests

for tolyl-specific serum IgE antibodies are not sufficiently sensitive or specific for use in medical screening or diagnosis of bronchial hypersensitivity in workers exposed to TDI.

• **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 TDI 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 (acute).
2. Delayed-onset SHE's include: Extrinsic asthma (chronic).

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to TDI 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 TDI. 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 TDI vapors using midget impingers filled with a solution of 1-(2-methoxy phenyl)-piperazine in toluene and analyzing by liquid chromatography with UV detection. Detector tubes or other direct-reading devices calibrated to measure TDI may also be used if available. A detailed sampling and analytical method for TDI may be found in the *NIOSH Manual for Analytical Methods* (method number 2535).

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 TDI.

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

SANITATION

Clothing which is contaminated with TDI 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 TDI from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of TDI's hazardous properties. Before being laundered, contaminated clothing shall be placed in a decontaminating solution of water containing 10% ammonia in a container that is impervious to TDI. Caution: Do not tightly close containers used for decontamination because of a possible increase in gas pressure.

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

Skin that becomes contaminated with TDI 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 TDI 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 TDI 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 toluene diisocyanate

Operations	Controls
During use in the manufacture of diisocyanatepolyol surface coatings and and finishes, polyurethane paints, and electrical and thermal insulation	Process enclosure, general dilution ventilation, local exhaust ventilation, personal protective equipment
During use in the manufacture and curing of flexible polyurethane foams and elastoplastics, adhesives, and sealants	Process enclosure, 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 TDI, an eye-wash fountain should be provided within the immediate work area for emergency use.

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

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

Condition	Minimum respiratory protection*†
Concentration:	
Less than or equal to 0.05 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 0.125 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 1 ppm	Any self-contained breathing apparatus with a full facepiece
	Any supplied-air respirator with a full facepiece
Less than or equal to 10 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 10 ppm	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic vapor 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 0.005 ppm (0.035 mg/m^3) (TWA) and 0.02 ppm (0.14 mg/m^3) (ceiling).

Occupational Health Guideline for o-Toluidine*

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: $CH_3C_6H_4NH_2$
- Synonyms: Ortho-aminotoluene; o-methylaniline; 1-methyl-2-aminobenzene; 2-methylaniline
- Appearance and odor: Colorless to pale yellow liquid with a weak, aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-toluidine is 5 parts of o-toluidine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 22 milligrams of o-toluidine 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 o-toluidine from 5 ppm to 2 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

o-Toluidine 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 o-toluidine may affect the ability of the blood to carry oxygen. The earliest effect from exposure to this chemical is a bluish discoloration of the lips, tongue, and finger nails. At first, if the oxygen lack is not severe, the exposed person may have a feeling of well being. As the lack of oxygen increases, effects such as drowsiness, headache, nausea, and vomiting may appear. If oxygen lack is very severe, it may cause unconsciousness and even death. Liquid toluidine is irritating to the eyes. Recovery from eye exposure may take a long time unless the eyes are flushed with water immediately. In addition, exposure to o-toluidine may cause bloody urine for a short time.

- **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-toluidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to o-toluidine 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. The skin should be examined for evidence of chronic disorders.

—A complete blood count: o-Toluidine has been shown to cause methemoglobinemia. 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.

—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.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determination should be performed when o-toluidine intoxication is suspected.

- **Summary of toxicology**

o-Toluidine absorption, whether from inhalation of the vapor or by skin absorption of the liquid, causes anoxia (due to the formation of methemoglobin), and hematu-

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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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U.S. DEPARTMENT OF LABOR
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September 1978

ria. The earliest manifestations of poisoning in humans are headache and cyanosis of the lips, the mucous membranes, the fingernail beds, and the tongue. Minor degrees of hypoxia may lead to a temporary sense of well-being and exhilaration. As the lack of oxygen increases, however, there is growing weakness, dizziness, and drowsiness, leading to stupor, unconsciousness, and death if treatment is not prompt. Transient microscopic hematuria has been observed in o-toluidine workers, presumably of renal origin, since no alterations in the bladder mucosa were observed by cystoscopy. In the eye of a rabbit, the liquid caused a severe burn. Excessive drying of the skin may result from repeated or prolonged contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 107
  2. Boiling point (760 mm Hg): 199.7 C (391 F)
  3. Specific gravity (water = 1): 1.00
  4. Vapor density (air = 1 at boiling point of o-toluidine): 3.7
  5. Melting point: −16.3 C (−3 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): 1.5
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving o-toluidine.
  4. Special precautions: Liquid o-toluidine will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 85 C (185 F) (closed cup)
  2. Autoignition temperature: 482 C (900 F)
  3. Flammable limits in air, % by volume: Lower: 1.5 (calculated at flash point)
  4. Extinguishant: Carbon dioxide, dry chemical, foam
- **Warning properties**
  1. Odor Threshold: The Manufacturing Chemists Association reports that o-toluidine has an aromatic, aniline-like odor, but no information is available concerning the odor threshold of this substance. Aniline, o-toluidine, and xylidine, however, represent a family of chemical compounds with increasing methyl substitution. Since aniline has an odor threshold of 7 ppm and xylidine has an odor threshold of 0.0048 ppm, it is reasonable to assume that the aniline-like odor of o-toluidine is detectable at a concentration between 0.0048 and 7 ppm.
  2. Eye Irritation Level: o-Toluidine vapor is not known to be an eye irritant.
  3. Evaluation of Warning Properties: Since the odor threshold of o-toluidine is probably near 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 o-toluidine in an adsorption tube containing silica gel, followed by desorption with ethanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure o-toluidine may be used. An analytical method for o-toluidine 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 o-toluidine.
- Clothing contaminated with o-toluidine should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of o-toluidine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-toluidine, the person performing the operation should be informed of o-toluidine's hazardous properties.

- Where exposure of an employee's body to liquid o-toluidine 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 o-toluidine should be removed immediately and not reworn until the o-toluidine 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 liquid o-toluidine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid o-toluidine, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with o-toluidine should be immediately washed or showered with soap or mild detergent and water to remove any o-toluidine.
- Eating and smoking should not be permitted in areas where liquid o-toluidine is handled, processed, or stored.
- Employees who handle liquid o-toluidine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in dye industry in manufacture of dyes and dye intermediates; use in chemical industry in manufacture of organic chemicals and chemical intermediates	Process enclosure; general dilution ventilation; personal protective equipment
Use as a reagent chemical in blood sugar determinations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid o-toluidine 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 o-toluidine gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid o-toluidine 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 o-toluidine, 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 o-toluidine has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the person to vomit by having him touch the back of his throat with his finger or by giving him large amounts of warm water. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If o-toluidine 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:

o-Toluidine 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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* SPECIAL NOTE

o-Toluidine 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 16, 1978.

RESPIRATORY PROTECTION FOR o-TOLUIDINE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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 Tributyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_4H_9O)_3PO$
- Synonyms: Tri-n-butyl phosphate; TBP
- Appearance and odor: Colorless to pale yellow, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tributyl phosphate is 5 milligrams of tributyl phosphate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for tributyl phosphate from 5 mg/m^3 to 2.5 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Tributyl phosphate can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Tributyl phosphate may cause irritation of the eyes, nose, and throat. It may also cause nausea and headache.

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 tributyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to tributyl phosphate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from tributyl phosphate exposure.

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

—Skin disease: Tributyl phosphate 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**

Tributyl phosphate vapor is a pulmonary irritant and, in animals, causes a moderate excitation of the nervous system. In rats, the oral LD50 is 3 g/kg; the effects are muscle twitching, weakness, dyspnea, and pulmonary edema. In vitro, tributyl phosphate causes weak inhibition of cholinesterases in human erythrocytes and plasma. Workers exposed to unspecified concentrations of vapor complained of headache and nausea; hot vapor was severely irritating to the eyes and throat. The liquid dropped on the eye of a rabbit caused temporary epithelial injury and discomfort. The liquid may be irritating to the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 266
  2. Boiling point (760 mm Hg): 293 C (560 F)
  3. Specific gravity (water = 1): 0.97
  4. Vapor density (air = 1 at boiling point of tributyl phosphate): 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: Less than −80 C (−112 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 0.1
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 phosphoric acid fume and carbon monoxide) may be released in a fire involving tributyl phosphate.
4. Special precautions: Liquid tributyl phosphate will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: 166 C (330 F) (closed cup)
2. Autoignition temperature: Higher than 482 C (900 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Carbon dioxide, dry chemical, foam

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of tributyl phosphate.
2. Eye Irritation Level: Grant states that tributyl phosphate, "tested on rabbit eyes by application of a drop, . . . had an effect similar to ethyl alcohol, causing temporary epithelial injury and pain, a reaction graded 3 on a scale of 1 to 10 after 24 hours, but no permanent injury." According to the *Hygienic Guide*, some eye irritation occurs at vapor concentrations of ethyl alcohol which are greater than 5500 ppm. Tributyl phosphate and ethyl alcohol in liquid form produce similar effects on the eye.
3. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties of tributyl phosphate to air concentrations, this substance is treated as having 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 tributyl phosphate on a filter, followed by extraction with ether, and gas chromatographic analysis. An analytical method for tributyl phosphate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid tributyl phosphate.

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

• Non-impervious clothing which becomes wet with liquid tributyl phosphate should be removed promptly and not reworn until the tributyl phosphate is removed from the clothing.

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

SANITATION

• Skin that becomes wet with liquid tributyl phosphate should be promptly washed or showered with soap or mild detergent and water to remove any tributyl phosphate.

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

Operation	Controls
Use as an antifoaming agent or plasticizer in manufacture of surface coatings and adhesives for latex exterior paints, pigment coatings for paper, inks, lacquers, and synthetic enamel finishes, and during milling pigments	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent in extraction of metals, including uranium, tharium, and rare earths in atomic energy processing	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a heat-exchange medium in aircraft engines	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 tributyl phosphate 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 tributyl phosphate gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid tributyl phosphate 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 tributyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When liquid tributyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

• If liquid tributyl phosphate 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:

Liquid tributyl phosphate 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 TRIBUTYL PHOSPHATE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate or Vapor Concentration	
50 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m³ or less	A gas mask with a chin-style or a front- or back-mounted organic vapor cartridge 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.
1300 mg/m³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 1300 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 1,1,2-Trichloroethane *

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: $CHCl_2CH_2Cl$
- Synonyms: Vinyl trichloride; beta-trichloroethane
- Appearance and odor: Colorless liquid with a sweet odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2-trichloroethane is 10 parts of 1,1,2-trichloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 45 milligrams of 1,1,2-trichloroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2-Trichloroethane 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: 1,1,2-Trichloroethane may cause irritation of the eyes and nose, drowsiness, incoordination, unconsciousness, and death. It might also cause liver and kidney damage.

2. Long-term Exposure: Repeated or prolonged exposure to 1,1,2-trichloroethane might cause liver or 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 1,1,2-trichloroethane.

- **Recommended medical surveillance**

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

—Liver disease: 1,1,2-Trichloroethane causes liver damage in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: 1,1,2-Trichloroethane causes kidney damage in animals and 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**

1,1,2-Trichloroethane vapor is a potent narcotic. Injury to lungs, liver, and kidneys has been observed in animals. The lethal concentration for rats was 2000 ppm for 4 hours. Concentrations resulting in narcosis also caused irritation of the nose and eyes. Mice treated by intraperitoneal injection with anesthetic doses showed moderate hepatic dysfunction and renal dysfunction; at autopsy, there was centrolobular necrosis of the liver and tubular necrosis of the kidney. No human cases of intoxication or systemic effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 133.4
2. Boiling point (760 mm Hg): 113 C (236 F)
3. Specific gravity (water = 1): 1.43
4. Vapor density (air = 1 at boiling point of 1,1,2-trichloroethane): 4.55
5. Melting point: −37 C (−34 F)
6. Vapor pressure at 20 C (68 F): 18.8 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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0.45

8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Heat.

2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as aluminum and magnesium powders, sodium or 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 1,1,2-trichloroethane.

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

• **Flammability**

1. Flash point: None in normal test method

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Lower: 6.0; Upper: 15.5 (high energy ignition source required)

4. Extinguishant: Foam, carbon dioxide, dry chemical

• **Warning properties**

1. Odor Threshold: Although 1,1,2-trichloroethane is known to have a sweet, chloroform-like odor, no quantitative data are available concerning the odor threshold of this substance.

2. Eye Irritation Level: Grant reports that high concentrations of the vapors are irritating to the eyes. The concentrations at which this irritation occurs are not stated.

3. Other Information: Grant reports that high concentrations of the vapors are irritating to the respiratory tract, but no quantitative information is given.

4. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties to air concentrations of 1,1,2-trichloroethane, this substance has been treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube 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 1,1,2-trichloroethane may be used. An analytical method for 1,1,2-trichloroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1,2-trichloroethane.

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

• Non-impervious clothing which becomes contaminated with liquid 1,1,2-trichloroethane should be removed promptly and not reworn until the 1,1,2-trichloroethane is removed from the clothing.

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

SANITATION

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

• Eating and smoking should not be permitted in areas where liquid 1,1,2-trichloroethane is handled, processed, or stored.
• Employees who handle liquid 1,1,2-trichloroethane 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 1,1,2-trichloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in organic synthesis in production of vinylidene chloride	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 1,1,2-trichloroethane 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 1,1,2-trichloroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2-trichloroethane 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 1,1,2-trichloroethane, 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 1,1,2-trichloroethane 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 1,1,2-trichloroethane 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, or a similar material.
• Waste disposal method:
1,1,2-Trichloroethane 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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* SPECIAL NOTE

1,1,2-Trichloroethane 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 20, 1979.

RESPIRATORY PROTECTION FOR 1,1,2-TRICHLOROETHANE

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.

OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR TRICHLOROETHYLENE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about trichloroethylene 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_2HCl_3
- **Structure:** $CCl_2 = CHCl$
- **Synonyms:** Acetylene trichloride, ethylene trichloride, TCE
- **Identifiers:** CAS 79-01-6; RTECS KX455000; DOT 1710, label required: "St. Andrew's Cross (X)"
- **Appearance and odor:** Colorless liquid with a sweet odor like chloroform

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 131.38
2. Boiling point (at 760 mmHg): 87.1°C (188°F)
3. Specific gravity (water = 1): 1.46
4. Vapor density (air = 1 at boiling point of trichloroethylene): 4.54
5. Melting point: -86.4°C (-123°F)
6. Vapor pressure at 25°C (77°F): 74.3 mmHg
7. Solubility in water, g/100 g water at 25°C (77°F): 0.00011
8. Evaporation rate (butyl acetate = 1): 6.2
9. Saturation concentration in air (approximate) at 25°C (77°F): 10.1% (101,000 ppm)
10. Ionization potential: 9.47 eV

- **Reactivity**

1. Incompatibilities: Trichloroethylene may react violently with chemically active metals such as barium, lithium, sodium, magnesium, and titanium. Aluminum may react with the free hydrogen chloride in trichloroethylene to produce aluminum chloride, which catalyzes a violent self-accelerating polymerization reaction. Contact with strong caustics may cause the formation of dichloracetylene, a toxic and flammable gas.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., phosgene, hydrogen chloride, and carbon monoxide) may be released in a fire involving trichloroethylene.

- **Flammability**

1. Flash point: 32°C (90°F) (closed cup)
2. Autoignition temperature: 788°C (420°F)
3. Flammable limits in air, % by volume: Lower, 12.5; Upper, 90
4. Extinguishant: Alcohol foam, dry chemical, or carbon dioxide
5. Class IC Flammable Liquid (29 CFR 1910.106), Flammability Rating 1, Practically Nonflammable (NFPA)

- **Warning properties**

1. Odor threshold: 21.4 ppm
2. Eye irritation level: 400 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 trichloroethylene per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift; the acceptable ceiling concentration is 200 ppm; and the maximum peak concentration above the acceptable ceiling (maximum duration of 5 minutes in any 2-hour period) is 300 ppm. The National Institute for Occupational Safety and Health (NIOSH) recommends that trichloroethylene be controlled and handled as a potential human carcinogen in the workplace and that exposure be minimized to the lowest feasible limit. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV®) is 50 ppm (270 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek; the ACGIH short-term exposure limit (STEL) is 200 ppm (1,080 mg/m³) (Table 1).

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Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for trichloroethylene

	Exposure limits ppm	mg/m³
OSHA PEL TWA	100	—
Acceptable ceiling	200	—
Maximum ceiling (5 min in 2 h)	300	—
NIOSH REL TWA (Ca)*	25	—
ACGIH TLV® TWA	50	270
STEL	200	1,080

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

HEALTH HAZARD INFORMATION

• Routes of exposure

Trichloroethylene 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 trichloroethylene by multiple species of animals caused depressed brain function, brain damage, liver and kidney injury, and death due to respiratory failure or cardiac arrest. In rats, rabbits, guinea pigs, and gerbils, chronic inhalation of trichloroethylene caused toxic effects on the nerves, increases in liver and kidney weights, and suppression of growth. Chronic oral administration of trichloroethylene to mice produced cancers of the liver and lungs, and chronic inhalation by female mice produced cancers of the lymph system and lungs.

2. *Effects on humans:* Acute inhalation or ingestion of trichloroethylene has caused reversible peripheral nerve degeneration, injury to the liver and kidneys and to the cardiovascular and gastrointestinal systems, depression of the central nervous system, coma, and sudden death due to respiratory failure, cardiac arrhythmia, or liver or kidney failure. Chronic exposure to trichloroethylene has caused damage to the liver, kidneys, and nervous system. The ingestion of alcohol, caffeine, and some prescription drugs has been found to potentiate the effects of trichloroethylene intoxication. A dermal response seen as a reddening of the face, neck, back, and shoulders (degreaser's flush) has occurred in chronically exposed workers following the ingestion of alcohol. Repeated immersion of the hands into liquid trichloroethylene has caused paralysis of the fingers.

• Signs and symptoms of exposure

1. *Short-term (acute):* Inhalation exposure to trichloroethylene can cause drowsiness, dizziness, headache, blurred vision, incoordination, mental confusion, flushed skin, tremors, nausea, vomiting, fatigue, and cardiac arrhythmia. Irritation of the skin, mucous membranes, and eyes can also occur.

2. *Long-term (chronic):* Exposure can cause headache, cough, double vision, impaired coordination and senses of touch and smell, anxiety, dizziness, giddiness, weakness, tremor, slowness of heartbeat, and intolerance to alcohol. Dryness of the skin, blisters, and dermatitis can also occur.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

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

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

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to trichloroethylene, 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 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 trichloroethylene 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 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 trichloroethylene. 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 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 trichloroethylene 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: Toxic hepatitis.

MONITORING AND MEASUREMENT PROCEDURES

• TWA exposure evaluation

Measurements to determine worker exposure to trichloroethylene 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 trichloroethylene 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 trichloroethylene may also be used if available. A detailed sampling and analytical method for trichloroethylene may be found in the *NIOSH Manual of Analytical Methods* (method number S336).

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 trichloroethylene.

SANITATION

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

Operations	Controls
During use as a cleaning solvent in cold cleaning and vapor degreasing operations	Process enclosure, local exhaust ventilation, personal protective equiment
During use as a scouring and cleaning agent in textile processing; during use in the extraction and purification of animal and vegetable oils in food and pharmaceutical industries; during use in chemical synthesis	Process enclosure, local exhaust ventilation
During use in the manufacture of adhesives, anesthetics and analgesics, and cleaning and polishing preparations	Process enclosure, local exhaust ventilation
During use as a fumigant and disintectant for seeds and grains	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 trichloroethylene, an eye-wash fountain should be provided within the immediate work area for emergency use.

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

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

1. Ventilate area of spill or leak.
2. For small quantities of liquids containing trichloroethylene, absorb on paper towels and place in an appropriate container.
3. Large quantities of liquids containing trichloroethylene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
4. Liquids containing trichloroethylene 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.**

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Table 3.—Respiratory protection for trichloroethylene

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 Trichloronaphthalene

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: $C_{10}H_5Cl_3$
- Synonyms: Halowax; Seekay wax; nibren wax
- Appearance and odor: Colorless to pale yellow solid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Trichloronaphthalene 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**

Exposure to trichloronaphthalene may cause an acne-like rash. It may also injure the liver, resulting in such effects as fatigue, dark urine, and yellow jaundice.

- **Reporting signs and symptoms**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to trichloronaphthalene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to trichloronaphthalene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and skin should be stressed.

—Liver function tests: Trichloronaphthalene may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Trichloronaphthalene vapor and dust are toxic to the liver and the skin. Rats exposed to a mixture of tri- and tetrachloronaphthalene at 11 mg/m^3, 16 hours daily for 2-½ months showed slightly swollen liver cells with granular cytoplasm. An industrial exposure to unknown concentrations caused a severe acne-form dermatitis (chloracne) in 50 workers (89% of the crew); initially there was pruritis, which progressed to an acute eczema and finally a subacute folliculitis of acne type affecting mainly the face, periorbital region, cheeks, and ears. Two workers experienced anorexia, nausea, and vertigo. No fatal cases of liver injury have been reported, but one instance of toxic hepatitis resulted from exposure to 3 mg/m^3.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 231.4
2. Boiling point (760 mm Hg): 304– 354 C (580–670 F)
3. Specific gravity (water = 1): 1.58
4. Vapor density (air = 1 at boiling point of trichloronaphthalene): 8.0
5. Melting point: 93 C (199 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

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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8. Evaporation rate (butyl acetate = 1): Much less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving trichloronaphthalene.

4. Special precautions: None known.

- **Flammability**

1. Flash point: 200 C (392 F) (open cup)

2. Autoignition temperature: None to boiling point

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

4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Since there are no quantitative data relating warning properties to air concentrations of trichloronaphthalene, this substance is treated as a material with poor warning properties. The concentration of trichloronaphthalene in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

Even though the AIHA *Hygienic Guide* states that "eye injury has not proved to be troublesome with the chloronaphthalenes," trichloronaphthalene is treated as an eye irritant for the purposes of this guideline, as a Koppers Corporation *Material Safety Data Sheet* states that the vapors or dust may irritate the eyes.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of trichloronaphthalene on a filter and in a bubbler containing iso-octane, followed by extraction with iso-octane, and gas chromatographic analysis. An analytical method for trichloronaphthalene 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 trichloronaphthalene.
- 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 trichloronaphthalene or liquids containing trichloronaphthalene.
- 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 trichloronaphthalene fumes from the heated material.
- Non-impervious clothing which becomes contaminated with molten trichloronaphthalene should be removed immediately and not reworn until the trichloronaphthalene is removed from the clothing.
- Non-impervious clothing which becomes contaminated with solid trichloronaphthalene or liquids containing trichloronaphthalene should be removed promptly and not reworn until the trichloronaphthalene is removed from the clothing.
- If employees' clothing may have become contaminated with solid trichloronaphthalene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with trichloronaphthalene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of trichloronaphthalene from the clothing. If the clothing is to be laundered or otherwise cleaned to

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

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of molten trichloronaphthalene contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid trichloronaphthalene or liquids containing trichloronaphthalene may contact the eyes.

SANITATION

- Workers subject to skin contact with trichloronaphthalene should wash with soap or mild detergent and water any areas of the body which may have contacted trichloronaphthalene at the end of each work day.
- Skin that becomes contaminated with trichloronaphthalene should be promptly washed or showered with soap or mild detergent and water to remove any trichloronaphthalene.
- Employees who handle trichloronaphthalene 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 trichloronaphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Use as an insulating material in pouring, dipping, and covering of electrical equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation during use of electrical equipment	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an inert component for resins or polymers as a flame-resistant, water-proofing, and fungicidal/insecticidal agent in coatings for wood, textiles, and paper	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in catalytic chlorination of naphthalene to produce tetrachloronaphthalene and trichloronaphthalene; as a filler to impart flame resistance and improve electrical resistance to polymers; manufacture of special lubricants	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive for cutting oil	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an additive to special lubricants in crankcase oil, lubricants for farm machinery, and as an extreme-pressure lubricant	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 trichloronaphthalene or liquids containing trichloronaphthalene 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 trichloronaphthalene 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 solid trichloronaphthalene or liquids containing trichloronaphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If trichloronaphthalene 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. If molten trichloronaphthalene 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 trichloronaphthalene, 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 trichloronaphthalene 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 trichloronaphthalene 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 flammable 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:

Trichloronaphthalene may be disposed of:

1. By making packages of trichloronaphthalene in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving 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 TRICHLORONAPHTHALENE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
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.
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. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for 1,2,3-Trichloropropane

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: $CH_2ClCHClCH_2Cl$
- Synonyms: Allyl trichloride; glycerol trichlorohydrin; glycerin trichlorohydrin; trichlorohydrin
- Appearance and odor: Colorless liquid with a strong acid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,2,3-trichloropropane is 50 parts of 1,2,3-trichloropropane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 300 milligrams of 1,2,3-trichloropropane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,2,3-Trichloropropane 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: 1,2,3-Trichloropropane may cause irritation of the eyes, nose, and throat. It might cause drowsiness and liver damage.

2. Long-term Exposure: 1,2,3-Trichloropropane might cause irritation from prolonged or repeated 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 1,2,3-trichloropropane.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 1,2,3-trichloropropane 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 1,2,3-trichloropropane exposure.

—Skin disease: 1,2,3-Trichloropropane is a skin irritant. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: 1,2,3-Trichloropropane is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although 1,2,3-trichloropropane 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 1,2,3-trichloropropane 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**

1,2,3-Trichloropropane vapor is a narcotic, irritates the upper respiratory tract, and is toxic to the liver. Inhalation by mice of 30 mg/liter (5,000 ppm) for 20 minutes was fatal to 8 of 15 exposed; liver damage accounted for four additional deaths 7 to 10 days later; daily 10-minute exposures at 2,500 ppm for 10 days resulted in 7 deaths among 10 mice. In rabbits the liquid was an intense skin irritant and caused erythema, sloughing, and cracking. In an experimental human study, exposure to 100 ppm

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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was objectionable because of eye and throat irritation and unpleasant odor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 147.4
  2. Boiling point (760 mm Hg): 156 C (313 F)
  3. Specific gravity (water = 1): 1.4
  4. Vapor density (air = 1 at boiling point of 1,2,3-trichloropropane): 5
  5. Melting point: −14.7 C (5 F)
  6. Vapor pressure at 20 C (68 F): 3.4 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 active metals, strong caustics, or 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 1,2,3-trichloropropane.
  4. Special precautions: 1,2,3-Trichloropropane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Flash point: 73.3 C (164 F) (closed cup)
  2. Autoignition temperature: 304 C (579 F)
  3. Flammable limits in air, % by volume: Lower: 3.2%; Upper: 12.6%
  4. Extinguishant: Foam, carbon dioxide, dry chemical
- **Warning properties**

The *Documentation of TLV's* reports that "the vapor of 1,2,3-trichloropropane was objectionable to all subjects exposed at a concentration of 100 ppm because of eye irritation, throat irritation, and unpleasant odor." Since this concentration is only twice the permissible exposure limit, this compound is considered to have adequate warning properties.

As mentioned above, the *Documentation of TLV's* states that 100 ppm causes eye irritation. However, this is not reported as a threshold level.

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 1,2,3-trichloropropane may be used. An analytical method for 1,2,3-trichloropropane 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 1,2,3-trichloropropane.
- Clothing contaminated with liquid 1,2,3-trichloropropane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,2,3-trichloropropane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,2,3-trichloropropane, the person performing the operation should be informed of 1,2,3-trichloropropane's hazardous properties.
- Where exposure of an employee's body to liquid 1,2,3-trichloropropane 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 1,2,3-trichloropropane should be re-

moved immediately and not reworn until the 1,2,3-trichloropropane 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 1,2,3-trichloropropane contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid 1,2,3-trichloropropane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with liquid 1,2,3-trichloropropane should be immediately washed or showered with soap or mild detergent and water to remove any 1,2,3-trichloropropane.

• Eating and smoking should not be permitted in areas where liquid 1,2,3-trichloropropane is handled, processed, or stored.

• Employees who handle liquid 1,2,3-trichloropropane 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 1,2,3-trichloropropane may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent and extractant for resins, oils, fats, waxes, and chlorinated rubber; as a commercial solvent for degreasing metal parts	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for the manufacture of other chemicals; use as a copolymer or telomer or cross-linking agent for sealing compounds	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If 1,2,3-trichloropropane 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 1,2,3-trichloropropane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,2,3-trichloropropane 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 1,2,3-trichloropropane, 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 1,2,3-trichloropropane 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 1,2,3-trichloropropane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

1,2,3-Trichloropropane 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: "1,2,3-Trichloropropane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR 1,2,3-TRICHLOROPROPANE

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).
	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.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of 1,2,3-trichloropropane; 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 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

Occupational Health Guideline for 1,1,2-Trichloro-1,2,2-Trifluoroethane

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-$CClF_2$
- Synonyms: Halocarbon 113; Refrigerant 113; TTE
- Appearance and odor: Colorless liquid with an odor like carbon tetrachloride (at high concentrations).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2-trichloro-1,2,2-trifluoroethane is 1000 parts of 1,1,2-trichloro-1,2,2-trifluoroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 7600 milligrams of 1,1,2-trichloro-1,2,2-trifluoroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

1,1,2-Trichloro-1,2,2-trifluoroethane 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: 1,1,2-Trichloro-1,2,2-trifluoroethane may cause irritation of the eyes and throat or drowsiness. Breathing high concentrations may cause the heart to beat irregularly or to stop.

2. Long-term Exposure: 1,1,2-Trichloro-1,2,2-trifluoroethane on prolonged or repeated contact with the skin may cause skin irritation.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2-trichloro-1,2,2-trifluoroethane.

- **Recommended medical surveillance**

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

—Skin disease: 1,1,2-Trichloro-1,2,2-trifluoroethane 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.

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrythmias, the breathing of 1,1,2-trichloro-1,2,2-trifluoroethane might cause exacerbation of symptoms due to its sensitizing properties.

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

- **Summary of toxicology**

1,1,2-Trichloro-1,2,2-trifluoroethane vapor is a narcotic. In guinea pigs exposed to 25,000 ppm, nasal irritation was rapidly apparent and incoordination occurred at 50,000 ppm after 30 minutes; death occurred after one hour at this level. In dogs, cardiac sensitization to epinephrine occurred at concentrations of 5,000 to 10,000 ppm. The liquid produced no irritation on the abraded or intact skin of guinea pigs; in the eyes of rabbits it produced mild conjunctivitis and minimal corneal dullness, which were reversible. In experimental human studies, exposure to 4,500 ppm for 30 to 100 minutes resulted in significant impairment in tests of manual dexterity and vigilance; subjects reported loss of concentration and a tendency to somnolence which disappeared 15 minutes after the exposure ended; at

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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1,500 ppm no effects were observed. More prolonged human exposures of 6 hours daily, 5 days per week for 2 weeks at concentrations of approximately 500 and 1,000 ppm resulted in no adverse effects, with the exception of mild throat irritation on the first day; there was no decrement in performance of complex mental tasks. The liquid dissolves the natural oils of the skin, and dermatitis may occur as a result of repeated contact.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 187.4
  2. Boiling point (760 mm Hg): 47.6 C (117.6 F)
  3. Specific gravity (water = 1): 1.55
  4. Vapor density (air = 1 at boiling point of 1,1,2-trichloro-1,2,2-trifluoroethane): 6.5
  5. Melting point: −35 C (−31 F)
  6. Vapor pressure at 20 C (68 F): 284 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.017
  8. Evaporation rate (butyl acetate = 1): Greater than 1
- **Reactivity**
  1. Conditions contributing to instability: Heat
  2. Incompatibilities: Reacts with chemically active metals such as calcium, powdered aluminum, zinc, magnesium and beryllium. Contact with magnesium alloys containing more than 2% magnesium may cause decomposition.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, hydrogen fluoride, phosgene, and carbon monoxide) may be released when 1,1,2-trichloro-1,2,2-trifluoroethane decomposes.
  4. Special precautions: 1,1,2-Trichloro-1,2,2-trifluoroethane will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Not combustible
- **Warning properties**

Since the AIHA *Hygienic Guide* states that this compound is "nearly odorless," and since experimental evidence indicates that its irritant effects are only slight and transient at concentrations near the permissible exposure, it is treated as a material with poor warning properties.

There is no evidence to indicate that the vapor is an eye irritant. The *Documentation of TLV's* states that "no corneal injury or irritation" was observed in guinea pigs exposed to this substance. For the purposes of this guideline, therefore, it is not treated as 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 1,1,2-trichloro-1,2,2-trifluoroethane may be used. An analytical method for 1,1,2-trichloro-1,2,2-trifluoroethane 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).

(order number PB 265 028).

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 1,1,2-trichloro-1,2,2-trifluoroethane.
- Non-impervious clothing which becomes wet with liquid 1,1,2-trichloro-1,2,2-trifluoroethane should be removed promptly and not reworn until the 1,1,2-trichloro-1,2,2-trifluoroethane 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 1,1,2-trichloro-1,2,2-trifluoroethane contacting the eyes.

SANITATION

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

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as a selective solvent in degreasing electrical equipment, photographic films, magnetic tapes, precision instruments, plastics, glass, elastomers, or metal components; as dry cleaning solvent for all fabrics, leather, and suedes.	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a refrigerant in commercial/industrial air conditioning and industrial process cooling	General dilution ventilation
Use as a chemical intermediate for dechloronization of chemicals in the manufacture of polymers, and copolymers in production of high-temperature lubricants	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a foaming or blowing agent in the manufacture of polymers for flame retardancy	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a solvent in the textile industry; and as a solvent in special laboratory usage	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 1,1,2-trichloro-1,2,2-trifluoroethane 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 1,1,2-trichloro-1,2,2-trifluoroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2-trichloro-1,2,2-trifluoroethane 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 1,1,2-trichloro-1,2,2-trifluoroethane, 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 1,1,2-trichloro-1,2,2-trifluoroethane 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 1,1,2-trichloro-1,2,2-trifluoroethane 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:

1,1,2-Trichloro-1,2,2-trifluoroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

REFERENCES

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

• American Industrial Hygiene Association: "1,1,2-Trichloro-1,2,2-Trifluoroethane," *Hygienic Guide Series*, Detroit, Michigan, 1968.

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RESPIRATORY PROTECTION FOR 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
4500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
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 Trifluoromonobromomethane

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: $CBrF_3$
- Synonyms: Halocarbon 13B1; Refrigerant 13B1; bromotrifluoromethane; Halon 1301
- Appearance and odor: Colorless gas with a slight ethereal odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for trifluoromonobromomethane is 1000 parts of trifluoromonobromomethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6100 milligrams of trifluoromonobromomethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Trifluoromonobromomethane can affect the body if it is inhaled. It may also affect the body if the liquid comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Breathing high concentrations of trifluoromonobromomethane may cause lightheadedness. Breathing very high concentrations of trifluoromonobromomethane may cause the heart to beat irregularly or stop.

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 trifluoromonobromomethane.

- **Recommended medical surveillance**

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

—Cardiovascular disease: In persons with impaired cardiovascular function, especially those with a history of cardiac arrythmias, the breathing of trifluoromonobromomethane might cause exacerbation of symptoms due to its sensitizing properties.

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

- **Summary of toxicology**

Trifluoromonobromomethane vapor is a narcotic at high concentrations. In dogs and rats repeatedly exposed to 23,000 ppm there were no toxic signs or pathologic changes. Monkeys exposed to concentrations of 20% (200,000 ppm) became lethargic and suffered spontaneous cardiac arrhythmias within 5 to 40 seconds of exposure. In animal exposure studies at high levels, sensitization of the myocardium to epinephrine was reported. In human experiments designed to determine the safety of the substance as a firefighting agent in airplane cabins, exposure of three volunteers at 7% (70,000 ppm) for three minutes produced no cardiac anomalies.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 149
2. Boiling point (760 mm Hg): −57.8 C (−72 F)
3. Specific gravity (water = 1): 1.54 at 77 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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4. Vapor density (air = 1 at boiling point of trifluoromonobromomethane): 5

5. Melting point: −168 C (−270 F)

6. Vapor pressure at 20 C (68 F): Not pertinent

7. Solubility in water, g/100 g water at 20 C (68 F): 0.03

8. Evaporation rate (butyl acetate = 1): Not pertinent

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Reacts with chemically active metals, calcium, or with powdered aluminum, zinc, and magnesium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide, carbonyl fluoride, hydrogen fluoride, and carbon monoxide) may be released when trifluoromonobromomethane decomposes.

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

• **Flammability**

1. Not combustible

• **Warning properties**

Trifluoromonobromomethane does not have adequate warning properties.

Trifluoromonobromomethane 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 vapors using an adsorption tube with subsequent desorption with 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 trifluoromonobromomethane may be used. An analytical method for trifluoromonobromomethane 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 trifluoromonobromomethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as commercial and military fire extinguishant; use as a refrigerant for food processing and storage; use as a blowing agent to improve flame retardancy of rigid polyurethane foams	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis in production of olefin resins; use during the manufacture of hydraulic fluids as an erosion inhibitor	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during use for special purposes in bubble chambers for ionization studies, in "quark" detection, and in radiation counters	General dilution ventilation; local exhaust ventilation; perosnal 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 trifluoromonobromomethane, 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 trifluoromonobromomethane is leaked, the following steps should be taken:

1. Ventilate area of leak.
2. Stop flow of gas.

REFERENCES

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

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RESPIRATORY PROTECTION FOR TRIFLUOROMONOBROMOMETHANE

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 mode or with a full facepiece, helmet, or hood operated in 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 Triethylamine

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: $(C_2H_5)_3N$
- Synonyms: None
- Appearance and odor: Colorless liquid with a fishy odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for triethylamine is 25 parts of triethylamine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 100 milligrams of triethylamine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Triethylamine 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: Triethylamine causes irritation of the eyes, nose, and throat. If the liquid is splashed in the eyes, it may cause severe eye damage.

2. Long-term Exposure: Repeated or prolonged exposure to triethylamine may cause skin and lung irritation. Heart, liver, and kidney damage have been reported in animal experiments.

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 triethylamine.

- **Recommended medical surveillance**

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

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

—Cardiovascular disease: Triethylamine causes myocardial degeneration in animals. In persons with impaired cardiovascular function, the inhalation of triethylamine might cause exacerbation of pre-existing disorders.

—Liver disease: Triethylamine 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: Triethylamine 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: Triethylamine 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.

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

- **Summary of toxicology**

Triethylamine vapor is a primary irritant of mucous membranes and eyes. Exposure to 1000 ppm for 4 hours was lethal to rats. Rabbits survived exposures to 100 ppm daily for 6 weeks, but showed pulmonary irritation, myocardial degeneration, and cellular necrosis 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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U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

liver and kidney; at 50 ppm the effects on lung, liver, and kidney were less severe, but there was also damage to the cornea. In the eye of a rabbit, 1 drop of liquid triethylamine caused severe injury. Eye irritation and corneal edema in humans have been reported from industrial exposure. Closely related amines cause skin irritation.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 101.2
2. Boiling point (760 mm Hg): 89.5 C (193 F)
3. Specific gravity (water = 1): 0.73
4. Vapor density (air = 1 at boiling point of triethylamine): 3.5
5. Melting point: −115 C (−175 F)
6. Vapor pressure at 20 C (68 F): 54 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 5.5
8. Evaporation rate (butyl acetate = 1): 5.6

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

- **Flammability**

1. Flash point: −6.7 C (20 F) (closed cup)
2. Autoignition temperature: 450 C (842 F)
3. Flammable limits in air, % by volume: Lower: 1.2; Upper: 8.0
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Grant reports that triethylamine has a "strong ammoniacal odor," but no quantitative information concerning the odor threshold is available.
2. Eye Irritation Level: Grant reports that "chronic exposure of rabbits to triethylamine vapors at concentrations as low as 50 ppm in air causes multiple erosions of the cornea and conjunctiva . . . in the course of 6 weeks."
3. Other Information: Patty reports that rabbits repeatedly exposed to 50 ppm triethylamine over a 6-week period experienced lung irritation.
4. Evaluation of Warning Properties: Since information concerning the odor threshold is not available, and since the only quantitative information concerning its irritant effects is from chronic exposures, triethylamine 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 triethylamine 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 triethylamine may be used. An analytical method for triethylamine 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 triethylamine.
- Clothing wet with liquid triethylamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of

triethylamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the triethylamine, the person performing the operation should be informed of triethylamine's hazardous properties.

- Where exposure of an employee's body to liquid triethylamine 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 triethylamine or non-impervious clothing which becomes contaminated with triethylamine should be removed immediately and not reworn until the triethylamine 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 triethylamine or liquids containing triethylamine contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid triethylamine or liquids containing 1% or more of triethylamine by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with triethylamine should be immediately washed or showered to remove any triethylamine.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use in polymer technology as a catalyst for curing epoxy resins, for polyurethane foams, and for thermosetting polymers; as a stabilizing agent and chain-transfer agent; use in preparation of film-forming resins, as a solvent, pH stabilizer, and to improve water solubility in polymers	Local exhaust ventilation; general dilution ventilation
Use in extraction and purification of antibiotics; use in herbicides and pesticides, and in preparation of emulsifiers for pesticides	Local exhaust ventilation; general dilution ventilation
Use in organic synthesis of quarternary ammonium compounds in textile-treating chemicals, emulsifiers, surfactants, in paper manufacture, non-nutritive sweeteners, ketenes, and salts	Local exhaust ventilation; general dilution ventilation
Use as a corrosion inhibitor and chemical stabilizer for chlorinated solvents, in transmission fluids, oil well piping, engine parts, and gum inhibitors for gasoline	Local exhaust ventilation; general dilution ventilation
Use in paints and coatings to control viscosity and to prevent livering; to develop water resistance in resins; as a pH stabilizer; and to improve gloss of appliance finishes	Local exhaust ventilation; general dilution ventilation
Use as a dye assist; miscellaneous uses in rocket fuels to shorten ignition delays; ingredient of photographic development accelerator, for drying of printing inks, and in carpet cleaners	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 triethylamine or liquids containing triethylamine 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 triethylamine gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If triethylamine 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 triethylamine, 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 triethylamine 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 triethylamine 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. Triethylamine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Triethylamine 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 TRIETHYLAMINE

Condition	Minimum Respiratory Protection* Required Above 25 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 gas mask providing protection against triethylamine. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Trinitrotoluene

INTRODUCTION

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SUBSTANCE IDENTIFICATION

- Formula: $CH_3C_6H_2(NO_2)_3$
- Synonyms: TNT; trinitrotoluol; 2,4,6-trinitrotoluene; sym-trinitrotoluene
- Appearance and odor: Colorless to pale yellow, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for trinitrotoluene is 1.5 milligrams of trinitrotoluene per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for trinitrotoluene a Threshold Limit Value of 0.5 mg/m³ with a skin notation.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Trinitrotoluene 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 trinitrotoluene can cause liver damage with yellow jaundice and anemia which may be fatal. It may also cause irritation of the eyes, nose, and throat with sneezing, cough, and sore throat. It may cause a skin rash and stain the skin, hair, and nails a yellowish color. It may affect the ability of the blood to carry oxygen. This may result in a bluish discoloration of the skin, weakness, drowsiness, shortness of breath and unconsciousness. In addition, it may cause muscular pains, heart irregularities, kidney irritation, cataracts of the eyes, menstrual irregularities, and nerve 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 trinitrotoluene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to trinitrotoluene 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 trinitrotoluene would be expected to be at increased risk from exposure. Examination of the blood, liver, eyes, cardiovascular system, nervous system, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Trinitrotoluene has been shown to cause aplastic anemia in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Liver function tests: Since liver damage has been observed in humans exposed to trinitrotoluene, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has been observed in humans exposed to trinitrotoluene, 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.

- **Summary of toxicology**

Trinitrotoluene (TNT) dust or fume causes liver

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, aplastic anemia, cyanosis, and dermatitis. There have been numerous fatalities of workers exposed to TNT in munitions plants; in a series of 22 fatal cases, 8 died from toxic hepatitis, 13 from aplastic anemia, and 1 from a combination of both. The vapor or dust can cause irritation of mucous membranes, resulting in sneezing, cough, and sore throat. Although intense or prolonged exposure to TNT may cause some cyanosis, it is not regarded as a strong producer of methemoglobin. Other occasional effects are leukocytosis or leukopenia, peripheral neuritis, muscular pains, cardiac irregularities, and renal irritation. Cataracts have been observed in a considerable proportion of chronically exposed workers; one report indicates that 26 of 61 workers with an average exposure of 8.4 years had a characteristic peripheral cataract. TNT causes sensitization dermatitis; the hands, wrists, and forearms are most commonly affected, but skin at friction points such as the collar line, belt line, and ankles is also often involved; erythema, papules, and an itchy eczema can be severe. The skin, hair, and nails of exposed workers may be stained yellow.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 227
2. Boiling point (760 mm Hg): 240 C (464 F) (explodes)
3. Specific gravity (water = 1): 1.65
4. Vapor density (air = 1 at boiling point of trinitrotoluene): Not applicable
5. Melting point: 81 C (178 F)
6. Vapor pressure at 85 C (185 F): 0.053 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.013
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Slow decomposition occurs above 180 C (356 F). Exposure to light may increase impact sensitivity. Rapid heating may cause detonation.
2. Incompatibilities: Contact with strong oxidizers may cause fire. Contact with ammonia or with strong alkalies may increase sensitivity to shock. Can react vigorously with oxidizable materials.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving trinitrotoluene.
4. Special precautions: Protect from shock.

- **Flammability**

1. Flash point: Explodes
2. Impact sensitivity (minimum fall of a 2 kg weight to cause at least one explosion in ten trials): 100 cm
3. Explosion temperature (temperature required to cause explosion in five seconds): 475 C (887 F)
4. Extinguishant: Water may be used on small fires. Do not attempt to extinguish large fires.

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of TNT.
2. Eye Irritation Level: Grant states that "irritation of the eyes and skin is not uncommon among munitions workers exposed to its dust and fumes." No quantitative information is available concerning the air concentrations which produce the eye irritation.
3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of TNT, this substance is treated as a material with poor warning properties. The concentration in saturated air at 20 C might 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**

At the time of publication of this guideline, no measurement method for trinitrotoluene 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 trinitrotoluene or liquids containing trinitrotoluene.

• If employees' clothing may have become contaminated with solid trinitrotoluene, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with trinitrotoluene should be removed promptly and not reworn until the trinitrotoluene is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where solid trinitrotoluene or liquids containing trinitrotoluene may contact the eyes.

SANITATION

• Workers subject to skin contact with solid trinitrotoluene or liquids containing trinitrotoluene should wash with soap or mild detergent and water any areas of the body which may have contacted trinitrotoluene at the end of each work day.

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

• Eating and smoking should not be permitted in areas where solid trinitrotoluene or liquids containing trinitrotoluene are handled, processed, or stored.

• Employees who handle solid trinitrotoluene or liquids containing trinitrotoluene 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 trinitrotoluene may occur and control methods which may be effective in each case:

Operation	Controls
Use in the manufacture of shells, bombs, grenades, and mines; use in commercial explosives, and propellant compositions	Process enclosure; local exhaust ventilation; personal protective equipment
Use in the production of intermediates for synthesis of dyestuffs 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 trinitrotoluene or liquids containing trinitrotoluene 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 trinitrotoluene or liquids containing trinitrotoluene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If trinitrotoluene or liquids containing trinitrotoluene 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 trinitrotoluene, 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 trinitrotoluene or liquids containing trinitrotoluene 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 trinitrotoluene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Attempt to reclaim spilled material; however, do not sweep or burn unless this is supervised by explosives experts.

• Waste disposal method:

Trinitrotoluene may be disposed of only by explosives experts.

REFERENCES

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

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RESPIRATORY PROTECTION FOR TRINITROTOLUENE

Condition	Minimum Respiratory Protection* Required Above 1.5 mg/m³
Particulate or Vapor Concentration	
15 mg/m³ or 1.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
75 mg/m³ or 7.5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
3000 mg/m³ or 300 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 mg/m³ or 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 organic vapors and particulates. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Triorthocresyl 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: $(CH_3C_6H_4O)_3PO$
- Synonyms: O-tritolyl phosphate; TCP; TOCP
- Appearance and odor: Colorless, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for triorthocresyl phosphate is 0.1 milligram of triorthocresyl phosphate per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Triorthocresyl phosphate 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**

Triorthocresyl phosphate may cause paralyses of the lower arms and legs if it is swallowed, inhaled (as a fog mist, or aerosol), or absorbed through the skin. Nausea, vomiting, diarrhea, and abdominal pain may occur shortly after exposure. These symptoms disappear and are followed, after a symptom-free period of 3 to 28 days, by the paralytic effect.

- **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 triorthocresyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to triorthocresyl 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. Examination of the peripheral and central nervous systems should be stressed.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Triorthocresyl phosphate (TOCP) causes peripheral neuropathy with flaccid paralysis of the distal muscles of the upper and lower extremities, followed in some cases by a spastic paralysis. In affected cats and hens, extensive damage is observed in the spinal cord and sciatic nerves; damage to the myelin sheath and Schwann cells is secondary to the destructive lesion in the axon, which starts at the distal end of the longer axons. Thousands of people have been poisoned by the accidental ingestion of TOCP in contaminated foods and beverages; reports of intoxication from occupational exposure are rare. Shortly after ingestion there may be nausea, vomiting, diarrhea, and abdominal pain. After a symptom-free interval of 3 to 28 days, most patients complain of sharp, cramplike pains in the calf muscles, and some of numbness and tingling in the feet and sometimes the hands. Within a few hours there is increasing weakness of the legs and feet, progressing to bilateral footdrop. After an interval of another 10 days, weakness of the fingers and wristdrop develop, but the paralysis is not usually as severe as occurs in the feet and legs; this process does not extend above the elbows; the thigh muscles are infrequently involved. Sensory changes, if they occur, are minor. With severe intoxication, lesions of the anterior horn cells and the pyramidal

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

tracts may also occur. Muscular weakness may increase over a period of several weeks or months; recovery may take months or years, and in 25 to 30% of cases permanent residual effects remain, usually confined to the lower limbs. Fatalities are rare and occur principally in those who have taken large quantities of TOCP in a short period of time; autopsy of six human cases revealed involvement of anterior horn cells and demyelination of nerve cells. The lethal dose for humans by ingestion is about 1.0 g/kg; severe paralysis has been produced by ingestion of 6 to 7 mg/kg. In workers engaged in the manufacture of aryl phosphates (including up to 20% TOCP) and exposed to concentrations of aryl phosphates at 0.2 to 3.4 mg/m^3, there was some inhibition of plasma cholinesterase but no correlation of this effect with degree of exposure or with minor gastrointestinal or neuromuscular symptoms. No effects on the eyes or skin have been reported; TOCP is readily absorbed through the skin without local irritant effects.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 368
2. Boiling point (760 mm Hg): 410 C (770 F) (decomposes)
3. Specific gravity (water = 1): 1.17
4. Vapor density (air = 1 at boiling point of triorthocresyl phosphate): Not applicable
5. Melting point: −33 C (−27 F)
6. Vapor pressure at 20 C (68 F): Very low (0.02 mm Hg at 150 C (302 F))
7. Solubility in water, g/100 g water at 20 C (68 F): 0.00003
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume and carbon monoxide) may be released in a fire involving triorthocresyl phosphate.
4. Special precautions: Liquid triorthocresyl phosphate will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 225 C (437 F) (closed cup)
2. Autoignition temperature: 385 C (725 F)
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

Triorthocresyl phosphate (TOCP) 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 triorthocresyl phosphate on a filter, followed by extraction with ether, and gas chromatographic analysis. An analytical method for triorthocresyl phosphate is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid triorthocresyl phosphate.
- Clothing contaminated with triorthocresyl phosphate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of triorthocresyl phosphate from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the triorthocresyl phosphate, the person

performing the operation should be informed of triorthocresyl phosphate's hazardous properties.

• Non-impervious clothing which becomes contaminated with triorthocresyl phosphate should be removed promptly and not reworn until the triorthocresyl phosphate is removed from the clothing.

SANITATION

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

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

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

Operation	Controls
Use as a flame retarder and plasticizer in chlorinated rubber, nitrile rubber and resins; use in hot extrusion, molding, or bulk forming of plasticized polyvinyl chloride	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use in coatings and adhesives based on plasticized cellulose esters and alkyds	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a gasoline additive to control pre-ignition	Personal protective equipment
Use as a hydraulic fluid and a heat exchange medium	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as a synthetic lubricant; as a waterproofing agent; as a primary component of adhesives for air filter media; use as a solvent mixture for nitrocellulose and other natural resins	Personal protective equipment
Use as an extraction solvent in recovery of phenol from gas-plant effluents and coke-oven waste waters	Personal protective equipment
Use in grinding media for pigments; use as an intermediate in synthesis of pharmaceuticals	General dilution ventilation; 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 liquid triorthocresyl phosphate 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 triorthocresyl phosphate gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid triorthocresyl phosphate 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 triorthocresyl phosphate, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When liquid triorthocresyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency

rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

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

• If liquid triorthocresyl phosphate 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:

Liquid triorthocresyl phosphate 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 TRIORTHOCRESYL PHOSPHATE

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust and mist respirator, except single-use.
1 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.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	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 Triphenyl Phosphate

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $(C_6H_5O)_3PO$
- Synonyms: TPP; phenyl phosphate
- Appearance and odor: Colorless solid with a faint aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Triphenyl phosphate can affect the body if it is inhaled. It may also affect the body if it is swallowed.

- **Effects of overexposure**

Repeated exposure may cause minor changes in the blood enzymes. Animal exposures have produced muscle weakness and paralysis. These effects have not been reported in man.

- **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 triphenyl phosphate.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to triphenyl phosphate at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from triphenyl phosphate exposure.

—Neuromuscular disorders: Triphenyl phosphate causes neurotoxic effects in animals. Persons with pre-existing neuromuscular disorders 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**

Triphenyl phosphate is a neurotoxin in animals. When injected in cats it caused delayed paralysis. Two of 6 cats given a single intraperitoneal injection of triphenyl phosphate at 0.1 to 0.4 g/kg developed paralysis after 16 to 18 days. A group of 11 workers exposed to vapor, mist, or dust at an average concentration of 3.5 mg/m^3 and occasionally as high as 40 mg/m^3 for 8 to 10 years exhibited no signs of illness; the only positive finding was a slight but statistically significant reduction in erythrocyte cholinesterase activity. In workers engaged in the manufacture of aryl phosphates (including triphenyl phosphates and up to 20% triorthocresyl phosphate) and exposed to concentrations of aryl phosphates of 0.2 to 3.4 mg/m^3, there was some inhibition of plasma cholinesterase but no correlation of this effect with degree of exposure or with minor gastrointestinal or neuromuscular symptoms. The effects of triphenyl phosphate on the eye have not been reported; application in ethanol to the skin of mice produced no more irritation than was expected from the solvent.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 326
2. Boiling point (760 mm Hg): 370 C (698 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of triphenyl phosphate): Not applicable
5. Melting point: 48.5 C (119 F)
6. Vapor pressure at 20 C (68 F): Very low (0.15 mm

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

Hg at 150 C (302 F))

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: None hazardous

2. Incompatibilities: None

3. Hazardous decomposition products: Toxic gases and vapors (such as phosphoric acid fume and carbon monoxide) may be released in a fire involving triphenyl phosphate.

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

• **Flammability**

1. Flash point: 220 C (428 F) (closed cup)

2. Autoignition temperature: Data not available

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

4. Extinguishant: Carbon dioxide, dry chemical, foam

• **Warning properties**

Triphenyl phosphate 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 triphenyl phosphate on a filter, followed by extraction with ether, and gas chromatographic analysis. An analytical method for triphenyl phosphate is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use as a flame-retardant and plasticizer in compounding of chlorinated rubber; use on coatings and adhesives	General dilution ventilation; process enclosure; local exhaust ventilation
Use in hot extrusion, molding, or other bulk forming plasticized cellulose acetates	General dilution ventilation; process enclosure; local exhaust ventilation
Use as a fireproofing agent in manufacture of roofing paper	General dilution ventilation; 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.

• **Breathing**

If a person breathes in large amounts of triphenyl 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 triphenyl phosphate has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

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

• If triphenyl phosphate 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:

Triphenyl phosphate may be disposed of:

1. By making packages of triphenyl phosphate in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving triphenyl phosphate in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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

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RESPIRATORY PROTECTION FOR TRIPHENYL 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.
30 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.
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.
1500 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 1500 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 Turpentine

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: $C_{10}H_{16}$ (approximately); minimum alpha-pinene content 40% by weight
- Synonyms: Gum spirits of turpentine; turps; wood turpentine; spirits of turpentine; sulfate wood turpentine; sulfate turpentine; gum turpentine; steam-distilled turpentine
- Appearance and odor: Colorless liquid with a characteristic, paint odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for turpentine is 100 parts of turpentine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 560 milligrams of turpentine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Turpentine 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: Overexposure to turpentine may cause irritation of the eyes, nose, throat, lungs, and skin. It may also cause headache, dizziness, and painful urination or dark-red urine. Greater exposure may cause unconsciousness and death.

2. Long-term Exposure: Prolonged overexposure causes skin irritation. Skin sensitization can 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 turpentine.

- **Recommended medical surveillance**

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

—Skin disease: Turpentine is a skin defatting agent and sensitizer 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 turpentine 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: Turpentine has been reported to cause albuminuria and hematuria in humans and special consideration should be given to those with a history of impaired renal function.

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

Turpentine vapor is a mucous membrane irritant and, at higher concentrations, a convulsant. The LC50 for rats is 3590 ppm for 1 hour and 2150 ppm for 6 hours; hyperpnea, ataxia, tremors, and convulsions were noted. In cats, 1440 ppm produced disturbances in equilibrium and convulsions in 30 to 60 minutes; paralysis occurred in 150 to 180 minutes. In human subjects,

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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750 to 1000 ppm for several hours caused irritation of the eyes, headache, dizziness, nausea, and tachycardia; 1878 ppm for 1 to 4 hours was considered definitely toxic. Heavy overexposure is also reported to cause irritation of the nose and throat, cough, headache, vertigo, and irritation of the kidneys and bladder manifested by transient albuminuria and hematuria. However, there is little evidence that turpentine vapor at lower concentrations is a chronic systemic poison. Liquid in the eye causes conjunctivitis and corneal burns; a vapor concentration of 75-200 ppm is said to be moderately irritating. The liquid is also a defatting agent and causes skin irritation. Some persons may develop skin hypersensitivity. Mild intoxication from skin absorption has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 136 (approximately)
2. Boiling point (760 mm Hg): 150 to 180 C (302 to 356 F)
3. Specific gravity (water = 1): 0.864
4. Vapor density (air = 1 at boiling point of turpentine): 4.7
5. Melting point: −50 to −60 C (−58 to −76 F)
6. Vapor pressure at 25 C (77 F): 5 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 (especially chlorine) may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving turpentine.
4. Special precautions: Turpentine will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 35 C (95 F) (closed cup)
2. Autoignition temperature: 253 C (488 F)
3. Flammable limits in air, % by volume: Lower: 0.8
4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: Patty states that "the odor of 200 ppm turpentine in air is readily noticeable."
2. Eye Irritation Level: Patty states that 200 ppm "is moderately irritating to the eyes and mucous membranes of the nasal passages."
3. Evaluation of Warning Properties: Through its odor and irritant effects, turpentine can be detected at a level within twice the permissible exposure limit. For the purposes of this guideline, turpentine 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 turpentine 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 turpentine may be used. An analytical method for turpentine 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 turpentine.
- Clothing wet with liquid turpentine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of turpentine from the clothing. If the clothing is to be laundered or

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

- Any clothing which becomes wet with liquid turpentine should be removed immediately and non-impervious clothing which becomes contaminated with turpentine should be removed promptly and such clothing should not be reworn until the turpentine is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid turpentine may contact the eyes.

SANITATION

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

Operation	Controls
Use in manufacture of synthetic pine oil; insecticides; and in beta-pinene resins, flavors, and perfumes	Local exhaust ventilation; process enclosure; personal protective equipment
Use in preparation of polishes; use in manufacture of synthetic camphor, and use in paints	Local exhaust 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 turpentine 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 turpentine gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If turpentine 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 turpentine, 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 turpentine 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 turpentine 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. Turpentine should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Turpentine 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 TURPENTINE

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).
1900 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 1900 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 Uranium and Insoluble Compounds (as Uranium)

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 uranium and insoluble compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic uranium

- Formula: U
- Synonyms: None
- Appearance: Heavy, silvery white metal which is pyrophoric when finely divided.
- Note: U238 is radioactive with a half life of 4,900,000,000 years.

Uranium octaoxide

- Formula: U_3O_8
- Synonyms: Pitchblende
- Appearance and odor: Black, odorless solid.

Uranium tetrafluoride

- Formula: UF_4
- Synonyms: None
- Appearance and odor: Green, odorless solid.

Uranium hydride

- Formula: UH_3
- Synonyms: None
- Appearance: Brownish black or brownish gray powder.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for uranium or insoluble compounds is 0.25 milligram of uranium or insoluble compounds (as uranium) 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 uranium or insoluble compounds (as uranium) a Threshold Limit Value of 0.2 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Uranium or insoluble 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**

Exposure to insoluble uranium compounds has been reported to cause an increase in cancer of the lymphatic and blood-forming tissues in man. Prolonged contact with the skin might cause radiation damage to the skin. Prolonged inhalation of insoluble uranium compounds has caused damage to the lungs of 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 uranium or insoluble compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to uranium or insoluble 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. Exami-

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 of the respiratory system, blood, and lymphatic system should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Since uranium is deposited in the bone and is an alpha particle emitter, the function of the bone marrow is at 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.

—14" x 17" chest roentgenogram: Uranium or insoluble compounds cause lung damage in animals. Surveillance of the lungs is indicated.

—Urinalysis: Although not reported with insoluble uranium compounds, kidney damage has been reported due to uranium exposure. 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. In addition, a determination of urinary uranium levels should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

- **Summary of toxicology**

Insoluble compounds of uranium are less toxic than the soluble compounds. They are weakly radioactive and are principally alpha particle emitters; fibrotic changes have been observed in the lungs of animals after prolonged inhalation exposure, although radiation effects (other than possible carcinogenesis from absorbed uranium) have not been observed in humans. Both feeding and percutaneous toxicity studies on animals indicate that the insoluble uranium compounds are less toxic than the soluble compounds. Repeated exposures of three animal species to uranium dioxide dust at a concentration of 5 mg uranium/m^3 for periods up to 5 years resulted in no kidney injury; over 90% of the uranium found in the body was in the lungs and tracheobronchial lymph nodes (TLN). Fibrotic changes suggestive of radiation injury were seen occasionally in the TLN of dogs and monkeys and in the lungs of monkeys after exposure periods longer than 3 years; the estimated alpha dose to tissues was greater than 500 rads for lungs and 7000 rads for TLN. Rats injected with metallic uranium in the femoral marrow and in the chest wall developed sarcomata; whether this was due to metallocarcinogenic or radiocarcinogenic action could not be determined. The increased incidence of lung cancer reported among uranium miners is probably the result of exposure to radon gas and its particulate daughters, rather than to uranium dust. In a group of uranium mill workers, there was an excess of deaths from malignant disease of lymphatic and hematopoietic tissue; data from animal experiments suggested that this excess may have resulted from irradiation of lymph nodes by thorium-230, a disintegration product of uranium. Some absorbed uranium is deposited in bone; a potential risk of radiation effects on bone marrow has been postulated, but extensive clinical studies on exposed workers have disclosed no hematologic abnormalities. No evidence of chronic toxicity, either chemical or radiation, was observed for any uranium compound in the milling process during the first 6 years of the atomic energy program; all exposed workers were under very close medical surveillance. Prolonged skin contact with uranium compounds should be avoided because of potential radiation damage to basal cells; dermatitis has occurred as a result of handling uranium tetrafluoride.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Metallic uranium**
  1. Molecular weight: 238.03
  2. Boiling point (760 mm Hg): 3818 C (6904 F)
  3. Specific gravity (water = 1): 18.95
  4. Vapor density (air = 1 at boiling point of metallic uranium): Not applicable
  5. Melting point: 1133 C (2071 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—Uranium octaoxide**
  1. Molecular weight: 842.1
  2. Boiling point (760 mm Hg): Decomposes at 1300 C (2372 F)
  3. Specific gravity (water = 1): 7.31
  4. Vapor density (air = 1 at boiling point of uranium octaoxide): Not applicable
  5. Melting point: 1300 C (2372 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): Insoluble
  8. Evaporation rate (butyl acetate = 1):
- **Physical data—Uranium tetrafluoride**
  1. Molecular weight: 314
  2. Boiling point (760 mm Hg): 1417 C (2582 F) (sublimes)
  3. Specific gravity (water = 1): 6.7
  4. Vapor density (air = 1 at boiling point of uranium tetrafluoride): Not applicable
  5. Melting point: 969 C (1776 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—Uranium hydride**
  1. Molecular weight: 241
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): Data not available
  4. Vapor density (air = 1 at boiling point of uranium hydride): Not applicable
  5. Melting point: Decomposes
  6. Vapor pressure at 20 C (68 F): Essentially zero, except for decomposition products

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 (uranium hydride). Uranium turnings and fines stored out-of-doors in closed containers under water or water-soluble oil will partially convert into the hydride and eventually ignite during hot weather.

2. Incompatibilities: Contact of uranium with carbon dioxide, carbon tetrachloride, or nitric acid will cause fires or explosions. Contact of uranium hydride with strong oxidizers may cause fires and explosions. Contact of uranium hydride with water will form flammable and explosive hydrogen gas. Contact of uranium hydride with halogenated hydrocarbons can be violent.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen fluoride and carbon monoxide) may be released when uranium or insoluble compounds decompose.

4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable

2. Minimum ignition temperature: Uranium: 20 C (68 F) (cloud); 100 C (212 F) (layer); Uranium hydride: 20 C (68 F) (cloud); 20 C (68 F) (layer)

3. Minimum explosive concentration: 60 grams/m^3

4. Extinguishant: Dry powder, dry sand, graphite

• **Warning properties**

According to Grant, "several uranium compounds tested by dropping on the eyes of rabbits, guinea pigs, and rats have been found to cause severe eye damage as well as systemic poisoning. Compounds which have been found to cause moderately severe injury of the eyes are . . . uranium tetrafluoride, . . . uranium trioxide, uranium dioxide, and uranium peroxide . . . . The mildest damage was caused by the various uranium oxides."

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 uranium or insoluble compounds 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 solids or liquids containing uranium or insoluble compounds.

• If employees' clothing may have become contaminated with solids or liquids containing uranium or insoluble compounds, employees should change into uncontaminated clothing before leaving the work premises.

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

• Non-impervious clothing which becomes contaminated with uranium or insoluble compounds should be removed promptly and not reworn until the uranium or insoluble compounds are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solids or liquids containing uranium or insoluble compounds contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to solids or liquids containing uranium or insoluble compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with uranium or insoluble compounds should be promptly washed or showered with soap or mild detergent and water to remove any uranium or insoluble compounds.
- Eating and smoking should not be permitted in areas where solids or liquids containing uranium or insoluble compounds are handled, processed, or stored.
- Employees who handle solids or liquids containing uranium or insoluble 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 uranium or insoluble compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from mining, grinding, and milling of ores	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use of insoluble compounds as chemical intermediates in preparation of uranium compounds; use for nuclear technology	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in nuclear reactors as fuel and to pack nuclear fuel rods	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Liberation from burning of uranium metal chips and smelting operations	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in ceramics industry for pigments, coloring porcelain, painting on porcelain, and enamelling	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as catalysts for many reactions; in production of fluorescent glass	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 solids or liquids containing uranium or insoluble 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 solids or liquids containing uranium or insoluble compounds get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing uranium or insoluble compounds 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 uranium or insoluble 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 solids or liquids containing uranium or insoluble 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 PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If uranium or insoluble 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. Liquid containing uranium or insoluble compounds should be absorbed in vermiculite, dry sand, earth, or a similar material. Uranium chips or turnings which are spilled should be covered with oil.

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RESPIRATORY PROTECTION FOR URANIUM AND INSOLUBLE COMPOUNDS (AS URANIUM)

Condition	Minimum Respiratory Protection* Required Above 0.25 mg/m³
Particulate Concentration	
2.5 mg/m³ or less	Any fume respirator or high efficiency particulate filter respirator approved for radon daughters or radionuclides. Any supplied-air respirator. Any self-contained breathing apparatus.
12.5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
30 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 30 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Soluble Uranium Compounds (as Uranium)

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 uranium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Uranium hexafluoride

- Formula: UF_6
- Synonyms: None
- Appearance: Yellow, deliquescent solid.

Uranyl nitrate

- Formula: $UO_2(NO_3)_2$-$6H_2O$
- Synonyms: Uranium nitrate
- Appearance and odor: Yellow, odorless solid.

Uranyl sulfate

- Formula: UO_2SO_4-$3H_2O$
- Synonyms: None
- Appearance and odor: Yellow-green, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble uranium compounds is 0.05 milligram of soluble uranium compounds (as uranium) 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 soluble uranium compounds a Threshold Limit Value of 0.2 mg/m^3.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Soluble uranium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Soluble uranium compounds may cause irritation of the eyes with damage, lung damage, and kidney damage.

2. Long-term Exposure: Repeated or prolonged skin exposure to soluble uranium compounds may cause radiation damage to the skin. Exposure to soluble uranium compounds has been reported to cause an increase in cancer of the lymphatic and blood-forming tissues of man.

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 uranium compounds.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble uranium compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, blood, liver, lymphatic system, 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 uranium, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

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
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—A complete blood count: Since uranium is deposited in the bone and is an alpha-particle emitter, the function of the bone marrow should be monitored. 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. In addition, a determination of urinary uranium levels should be performed at any time overexposure is suspected or signs and symptoms of toxicity occur.

• **Summary of toxicology**

Soluble compounds of uranium as dust or mist are respiratory irritants and are toxic to the kidneys; uranium is weakly radioactive and emits alpha particles. Animals repeatedly exposed to dusts of soluble uranium compounds in concentrations from 3 to 20 mg/m^3 died of pulmonary and renal damage; both feeding and percutaneous toxicity studies on animals indicate that the more soluble compounds are the most toxic. In animals, effects on the liver are a consequence of the acidosis and azotemia induced by renal dysfunction. Rats injected with metallic uranium in the femoral marrow and in the chest wall developed sarcomata; whether this was due to metallocarcinogenic or radiocarcinogenic action could not be determined. The increased incidence of lung cancer reported among uranium miners is probably the result of exposure to radon gas and its particulate daughters, rather than to uranium dust. In a group of uranium mill workers there was an excess of deaths from malignant disease of lymphatic and hematopoietic tissue; data from animal experiments suggested that this excess may have resulted from irradiation of lymph nodes by thorium-230, a disintegration product of uranium. Some absorbed uranium is deposited in bone; a potential risk of radiation effects on bone marrow has been postulated, but extensive clinical studies on exposed workers have disclosed no hematologic abnormalities. Accidental exposure of workers to a mixture of uranium hexafluoride, uranium oxyfluoride, hydrofluoric acid, and live steam caused lacrimation, conjunctivitis, shortness of breath, paroxysmal cough, rales in the chest, nausea, vomiting, skin burns, transitory albuminuria, and elevation of blood urea nitrogen. The persons having the greatest exposure showed the highest urinary uranium levels; in addition, their urinary abnormalities were the most severe; these were albuminuria plus red cells and casts in the urinary sediment. Blood urea nitrogen remained elevated for several weeks. The injurious effects observed on the skin, eyes, and respiratory tract apparently were caused by the irritant action of the fluoride ion, whereas the uranium was responsible for the transient renal changes. No evidence of chronic toxicity, either chemical or radiation, was observed for any uranium compound during the first 6 years of the atomic energy program; all exposed workers were under very close medical surveillance. Soluble uranium compounds tested on the eyes of animals caused severe eye damage as well as systemic poisoning; the anion and its hydrolysis products determine the degree of injury. A hot nitric acid solution of uranyl nitrate spilled on the skin caused skin burns, nephritis, and encephalopathy. Prolonged skin contact with uranium compounds should be avoided because of potential radiation damage to basal cells; dermatitis has occurred as a result of handling uranium hexafluoride.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Uranium hexafluoride**

1. Molecular weight: 352
2. Boiling point (760 mm Hg): 56 C (133 F) (sublimes)
3. Specific gravity (water = 1): 4.68
4. Vapor density (air = 1 at boiling point of uranium hexafluoride): 12 (approximately)
5. Melting point: 65 C (149 F)
6. Vapor pressure at 20 C (68 F): 109 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Uranyl nitrate**

1. Molecular weight: 502.1
2. Boiling point (760 mm Hg): 118 C (244 F)
3. Specific gravity (water = 1): 2.8
4. Vapor density (air = 1 at boiling point of uranyl nitrate): Not applicable
5. Melting point: 60.2 C (140 F) (loses water)
6. Vapor pressure at 20 C (68 F): None, except water of crystallization
7. Solubility in water, g/100 g water at 20 C (68 F): 67
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Uranyl sulfate**

1. Molecular weight: 420.1
2. Boiling point (760 mm Hg): Decomposes at 100 C (212 F) (loses water)
3. Specific gravity (water = 1): 3.3
4. Vapor density (air = 1 at boiling point of uranyl sulfate): Not applicable
5. Melting point: 100 C (212 F) (loses water)
6. Vapor pressure at 20 C (68 F): None, except water of crystallization
7. Solubility in water, g/100 g water at 20 C (68 F): 70
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of uranyl nitrate with combustible material may cause fires and explosions. Uranium hexafluoride reacts with water to form hydrofluoric acid, a very corrosive substance.
3. Hazardous decomposition products: Toxic gases

and vapors (such as oxides of nitrogen and hydrofluoric acid) may be released in a fire involving soluble uranium compounds.

4. Special precautions: Uranium hexafluoride will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

Grant states that "several uranium compounds tested by dropping on the eyes of rabbits, guinea pigs, and rats have been found to cause severe eye damage as well as systemic poisoning. Compounds which have been found to cause moderately severe injury of the eyes are uranium pentachloride, uranium tetrachloride, uranyl nitrate, (and) uranyl fluoride . . . . Application of 1 mg of solid uranium pentachloride to the eyes of rabbits caused the most severe necrosis of conjunctivae and lids, and perforating ulceration of the cornea. The other chlorides and the nitrate were also severely damaging."

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 soluble uranium compounds 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 solids or liquids containing uranium hexafluoride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing soluble uranium compounds.
- If employees' clothing has had any possibility of being contaminated with uranium hexafluoride, or if employees' clothing may have become contaminated with other soluble uranium compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with uranium hexafluoride or clothing contaminated with other soluble uranium compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of soluble uranium compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the soluble uranium compounds, the person performing the operation should be informed of soluble uranium compounds's hazardous properties.
- Where there is any possibility of exposure of an employee's body to solids or liquids containing uranium hexafluoride, 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 uranium hexafluoride should be removed immediately and non-impervious clothing which becomes contaminated with other soluble uranium compounds should be removed promptly and not reworn until the soluble uranium compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solids or liquids containing soluble uranium compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solids or liquids containing soluble uranium compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with uranium hexafluoride should be immediately washed or showered and skin that becomes contaminated with soluble uranium compounds should be promptly washed or showered to remove any soluble uranium compounds.

• Workers subject to skin contact with solids or liquids containing uranium hexafluoride should wash any areas of the body which may have contacted uranium hexafluoride at the end of each work day.
• Eating and smoking should not be permitted in areas where solids or liquids containing soluble uranium compounds are handled, processed, or stored.
• Employees who handle solids or liquids containing soluble uranium compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during mining and purification of ore; during enrichment of elemental uranium; from recovery of process waste	Process enclosure; local exhaust ventilation; personal protective equipment
Use in fabrication of materials for military use and power plants	Process enclosure; local exhaust ventilation; personal protective equipment
Use as analytical reagents; use in chemical synthesis; use in manufacture of dyestuff intermediates and preparation of oxides	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of ceramic glazes; use as photographic intensifiers and in x-ray technology; in miccellaneous uses for textile printing, tobacco printing, antifungal agents, electroplating additives, and bacterial oxidants	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 solids or liquids containing soluble uranium 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 solids or liquids containing soluble uranium compounds get on the skin, immediately flush the contaminated skin with water. If solids or liquids containing soluble uranium compounds penetrate 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 soluble uranium 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 solids or liquids containing soluble uranium 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 PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
• If soluble uranium 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. Liquid containing soluble uranium compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

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RESPIRATORY PROTECTION FOR URANIUM SOLUBLE COMPOUNDS (AS URANIUM)

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m³
Particulate Concentration	
2.5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece (not applicable for uranium halides). A chemical cartridge respirator with a full facepiece, acid gas cartridge(s), and high efficiency particulate filter (for uranium halides only). A gas mask with a chin-style or a front- or back-mounted acid gas canister and high efficiency particulate filter (for uranium halides only). Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
20 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter (not applicable for uranium halides). A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with acid gas cartridge for uranium halides. Any gas mask providing protection against acid gases and particulates (for uranium halides only). Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Vanadium Pentoxide 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: V_2O_5
- Synonyms: None
- Appearance and odor: Yellow-orange powder or dark gray flakes with no odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for vanadium pentoxide dust is a ceiling of 0.5 milligrams of vanadium pentoxide dust per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 0.05 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Vanadium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Vanadium pentoxide dust 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: Vanadium pentoxide dust may cause irritation of the eyes, nose, throat, and respiratory tract. It may also cause bronchitis with wheezing and chest pain. A greenish discoloration of the tongue may occur.

2. Long-term Exposure: After symptoms have occurred following short-term exposure, repeated exposure may cause more severe symptoms of the same nature. In addition, repeated exposure may cause chronic bronchitis. Repeated or prolonged exposure may also cause an allergic 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 vanadium pentoxide dust.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to vanadium pentoxide 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 eyes and respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Vanadium pentoxide dust may cause respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Vanadium pentoxide 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. Vanadium in the urine may be evidence of absorption and excretion of this element since vanadium is not normally found in human urine.

- **Summary of toxicology**

Vanadium pentoxide dust is a respiratory and eye irritant. Sixteen workers exposed to concentrations of dust (and possibly some fume) in excess of 0.5 mg/m^3 with a mean particle size in the micron and submicron range developed conjunctivitis, nasopharyngitis, hacking cough, fine rales, and wheezing; in three workers exposed to the highest concentrations, the onset of symptoms occurred at the end of the first workday. 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.

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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bronchospastic element in the more seriously ill persisted for 48 hours after removal from exposure; rales lasted for 3 to 7 days, and in several cases cough lasted for up to 14 days. Among those with acute intoxication there was increased severity of symptoms from subsequent exposures of lesser time and intensity. Urinary vanadium excretion was detectable in 12 of the workers for periods of up to 2 weeks; vanadium in the urine may be evidence of absorption and excretion of this element, since vanadium is not ordinarily found in human urine. Workers exposed to a mixture of ammonium metavanadate and vanadium pentoxide at concentrations near 0.25 mg/m^3 developed green tongue, metallic taste, throat irritation, and cough. Another report of 36 workers examined 8 years after an acute respiratory reaction from vanadium pentoxide exposure indicated no evidence of either pneumoconiosis or emphysema, although six still had bronchitis with rhonchi resembling asthma and bouts of dyspnea. Two volunteers exposed to a concentration of 1 mg/m^3 for 8 hours developed a persistent cough which lasted for 8 days; 21 days after the original exposure, re-exposure for 5 minutes to a heavy cloud of vanadium pentoxide dust occurred, and within 16 hours marked cough developed; the following day, rales and expiratory wheezes were present throughout the entire lung field, but pulmonary functions were normal. Subjects exposed to a concentration of 0.2 mg/m^3 for 8 hours developed a loose cough the following morning; others exposed for 8 hours to 0.1 mg/m^3 developed slight cough with increased mucus which lasted 3 to 4 days. Both eyes and skin are irritated by the dust or by contact with an acid solution of vanadium pentoxide; eczematous lesions have occurred, and in three cases there was an allergic response to patch tests with sodium vanadate.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 181.9
  2. Boiling point (760 mm Hg): 1750 C (3182 F) (decomposes)
  3. Specific gravity (water = 1): 3.36
  4. Vapor density (air = 1 at boiling point of vanadium pentoxide dust): Not applicable
  5. Melting point: 690 C (1274 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.1
  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 ocmbustible
- **Warning properties**

According to Grant, vanadium pentoxide dust "causes a sensation of burning and irritation of the eyes, and signs of conjunctivitis . . . ." The eye irritation is accompanied by "irritation of the nose and throat. The respiratory irritation occurs at lower concentrations than does the ocular irritation. The local effects on the eye have also been observed in rabbits." The *Documentation of TLV's* states that "Gulko referred to eye and bronchial irritation from exposure at 0.5 to 2.2 mg/m^3."

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of vanadium pentoxide dust. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vanadium pentoxide dust on a mixed cellulose ester membrane filter, followed by chemical treatment and atomic desorption spectrophotometric analysis. An analytical method for vanadium pentoxide 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). ical Methods for Set 1" (order number PB 271 712).

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

SANITATION

- Skin that becomes contaminated with vanadium pentoxide dust should be promptly washed or showered to remove any vanadium pentoxide dust.
- Eating and smoking should not be permitted in areas where vanadium pentoxide dust is generated in the handling, processing, or storing of vanadium pentoxide.
- Employees who handle vanadium pentoxide dust should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation from cleaning and maintenance of furnaces, boilers, and gas turbines	Local exhaust ventilation; personal protective equipment
Liberation from mining and processing of ores; extraction from slag	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from use as a catalyst in the preparation of organic and inorganic compounds	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from chemical synthesis; use in manufacture of ultraviolet filter glass to prevent radiation injury and fading of fabrics	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from use in manufacture of afterburners for automobiles	Process enclosure; local exhaust ventilation (if possible); personal protective equipment
Liberation from use in textile industry as a catalyst to yield intensive black dyes; use in printing industry as a catalyst for formation of resinous black pigments from tar oils	Local exhaust ventilation
Liberation from use in ceramics industry in manufacture of ceramic pigments	Process enclosure; local exhaust ventilation
Liberation from use as a component of special steels in electric furnace steels, welding rods, and permanent magnets	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 vanadium pentoxide 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.

- **Skin Exposure**

If vanadium pentoxide dust gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If vanadium pentoxide dust penetrates 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 vanadium pentoxide dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When vanadium pentoxide dust 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 DISPOSAL PROCEDURES

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

• If vanadium pentoxide 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.

• Waste disposal method:

Vanadium pentoxide dust may be disposed of in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR VANADIUM PENTOXIDE DUST

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m³
Particulate Concentration	
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.
70 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 70 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 Vanadium Pentoxide 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: V_2O_5
- Synonyms: None
- Appearance: Finely divided particulates dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for vanadium pentoxide fume is a ceiling of 0.1 milligrams of vanadium pentoxide fume per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 0.05 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Vanadium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Vanadium pentoxide 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: Vanadium pentoxide fume may cause irritation of the eyes, nose, throat, and respiratory tract. It may also cause bronchitis with wheezing and chest pain. A greenish discoloration of the tongue may occur.

2. Long-term Exposure: After symptoms have occured following acute exposure, repeated exposure may cause more severe symptoms of the same nature. In addition, repeated exposure may cause chronic bronchitis. Repeated or prolonged exposure may cause an allergic 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 vanadium pentoxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to vanadium pentoxide 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 eyes and respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Vanadium pentoxide fume may cause respiratory impairment. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Vanadium pentoxide fume 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**

Vanadium pentoxide fume is a respiratory and eye irritant; the fume is recognized as being generally more toxic than dust of larger particle size, so similar effects from fume could be expected at lower concentrations. Sixteen workers exposed to concentrations of dust (and possibly some fume) in excess of 0.5 mg/m^3 with a mean particle size in the micron and submicron range developed conjunctivitis, nasopharyngitis, hacking cough, fine rales, and wheezing; in three workers exposed to the highest concentrations, the onset of symptoms occurred at the end of the first workday. 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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bronchospastic element in the more seriously ill persisted for 48 hours after removal from exposure; rales lasted for 3 to 7 days, and in several cases cough lasted for up to 14 days. Among those with acute intoxication there was increased severity of symptoms from subsequent exposures of lesser time and intensity. Urinary vanadium excretion was detectable in 12 of the workers for periods of up to 2 weeks; vanadium in the urine may be evidence of absorption and excretion of this element, since it is not ordinarily found in human urine. Workers exposed to a mixture of ammonium metavanadate and vanadium pentoxide at concentrations near 0.25 mg/m^3 developed green tongue, metallic taste, throat irritation, and cough. Another report of 36 workers examined 8 years after an acute respiratory reaction from vanadium pentoxide exposure indicated no evidence of either pneumoconiosis or emphysema, although six still had bronchitis with rhonchi resembling asthma and bouts of dyspnea. Two volunteers exposed to dust at a concentration of 1 mg/m^3 for 8 hours developed persistent cough which lasted for 8 days; 21 days after the original exposure, re-exposure for 5 minutes to a heavy cloud of vanadium pentoxide dust occurred, and within 16 hours marked cough developed; the following day, rales and expiratory wheezes were present throughout the entire lung field, but pulmonary functions were normal. Subjects exposed to dust at a concentration of 0.2 mg/m^3 for 8 hours developed a loose cough the following morning; others exposed for 8 hours to 0.1 mg/m^3 developed slight cough with increased mucus which lasted 3 to 4 days. Both eyes and skin are irritated by the dust or by contact with an acid solution of vanadium pentoxide; eczematous lesions have occurred, and in three cases there was an allergic response to patch tests with sodium vanadate.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 181.9
2. Boiling point (760 mm Hg): 1750 C (3182 F) (for solid)
3. Specific gravity (water = 1): 3.36 (for solid)
4. Vapor density (air = 1 at boiling point of vanadium pentoxide fume): Not applicable
5. Melting point: 690 C (1274 F) (for solid)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.1
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**

By analogy to vanadium pentoxide dust, which "causes a sensation of burning and irritation of the eyes and signs of conjunctivitis," according to Grant, vanadium pentoxide fume is treated as an eye irritant for the purposes of this guideline. The *Documentation of TLV's* states that "Gulko referred to eye . . . irritation from exposures at 0.5 to 2.2 mg/m^3" V_2O_5 dust.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of vanadium pentoxide fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vanadium pentoxide fume on a mixed cellulose ester membrane filter, followed by chemical treatment and atomic desorption spectrophotometric analysis. An analytical method for vanadium pentoxide fume 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).

• Zenz, C., and Berg, B. A.: "Human Responses to Controlled Vanadium Pentoxide Exposure," *Archives of Environmental Health*, 14:709-712, 1967.

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 vanadium pentoxide fume.
• Employees should be provided with and required to use dust-resistant safety goggles where vanadium pentoxide fume may contact the eyes.

SANITATION

• Eating and smoking should not be permitted in areas where vanadium pentoxide fume is generated in the handling, processing, or storing of vanadium pentoxide.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation from production of pellets from electric furnaces	Local exhaust ventilation; personal protective equipment
Liberation from fabrication of alloys for use as an additive in special steels	Local exhaust ventilation; personal protective equipment
Liberation from metallurgical processes in furnaces	Process enclosure
Liberation from manufacture of semiconductors fused with sodium oxide	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.
• **Breathing**
If a person breathes in large amounts of vanadium pentoxide 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 vanadium pentoxide fume are inadvertently released, ventilate the area of the release to disperse the fume.

ADDITIONAL INFORMATION

To find additional information on vanadium pentoxide fume, look up vanadium pentoxide fume in the following documents:
• Medical Surveillance for Chemical Hazards
• Respiratory Protection for Chemical Hazards
• Personal Protection and Sanitation for Chemical Hazards
• NIOSH Criteria Document for Vanadium (August 1977)
These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR VANADIUM PENTOXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 0.05 mg/m³
Particulate Concentration	
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
70 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 70 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 SAFETY AND HEALTH GUIDELINE FOR VINYL CHLORIDE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

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

SUBSTANCE IDENTIFICATION

- **Formula:** C_2H_3Cl
- **Structure:** $CH_2=CHCl$
- **Synonyms:** Chlorethene, chlorethylene, monochlorethylene, chloroethylene
- **Identifiers:** CAS 75-01-4; RTECS KU9625000; DOT 1086, label required: "Flammable Gas"
- **Appearance and odor:** Colorless gas with a sweet odor

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 62.50
2. Boiling point (at 760 mmHg): -14°C (7°F)
3. Specific gravity (water = 1): 0.9121
4. Vapor density (air = 1 at boiling point of vinyl chloride): 2.15
5. Melting point: -155.7°C (-243.4°F)
6. Vapor pressure at 20°C (68°F): 2,580 mmHg
7. Solubility in water, g/100 g water at 24°C (75°F): 0.11
8. Ionization potential: 9.995 eV

- **Reactivity**

1. Incompatibilities: Atmospheric oxygen and strong oxidizers may react with vinyl chloride to produce peroxide, which can initiate a violent polymerization reaction.
2. Hazardous decomposition products: Toxic vapors and gases (e.g., hydrogen chloride and carbon monoxide) may be released in a fire involving vinyl chloride.
3. Caution: Check valves for leaks.

- **Flammability**

1. Flash point: -78°C (-108°F) (open cup)
2. Autoignition temperature: 472°C (882°F)
3. Flammable limits in air, % by volume: Lower, 3.6; Upper, 33.0
4. Class IA Flammable Liquid Gas (29 CFR 1910.106), Flammability Rating 4 (NFPA)

- **Warning properties**

1. Odor threshold: 3,000 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 vinyl chloride is 1 part of vinyl chloride per million parts of air (ppm) as a time-weighted average (TWA) concentration over an 8-hour workshift, and the ceiling concentration which shall at no time be exceeded is 5 ppm as determined in any 15-minute sampling period. The National Institute for Occupational Safety and Health (NIOSH) recommends that vinyl chloride be controlled and handled as a potential human carcinogen in the workplace, and the NIOSH recommended exposure limit (REL) is that exposure be minimized to the lowest feasible limit. The American Conference of Governmental Industrial Hygienists (ACGIH) has designated vinyl chloride as an A1 substance (suspected human carcinogen) with an assigned threshold limit value, TLV® of 5 ppm [10 milligrams of vinyl chloride per cubic meter of air (mg/m^3)] as a TWA for a normal 8-hour workday and a 40-hour workweek (Table 1).

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Public Health Service Centers for Disease Control
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Division of Standards Development and Technology Transfer

Table 1.—Occupational exposure limits for vinyl chloride

	Exposure limits	
	ppm	mg/m³
OSHA PEL TWA	1	—
Ceiling (15 min)	5	—
NIOSH REL (Ca)*	Lowest feasible limit	
ACGIH TLV® TWA (Ala)†	5	10

* (Ca): NIOSH recommends treating as a potential human carcinogen.
† (Ala): Human carcinogen with an assigned TLV.

HEALTH HAZARD INFORMATION

• Routes of exposure
Vinyl chloride 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 vinyl chloride by multiple species of animals caused central nervous system depression, coma, and death; acute inhalation by dogs also caused cardiac arrhythmias. In mice, rats, and hamsters, chronic inhalation or oral administration of vinyl chloride produced cancers of the liver, kidney, central nervous system, skin, and mammary and ear duct glands.
2. *Effects on humans:* Acute exposure of workers to vinyl chloride has caused narcotic and anesthetic effects. Repeated exposure of workers to vinyl chloride has caused increased blood pressure, decreased blood platelet counts, increased liver enzyme levels, restricted blood flow, bone degeneration in the fingers, liver and spleen enlargement, nervous system disturbances, central nervous system depression, decreased respiratory function, and emphysema. Cancer of the liver has been associated with exposure of workers to vinyl chloride during the polyvinyl chloride production process. Cancers of the lung, brain, skin, nervous system, gall bladder, mouth, and pharynx have also been observed in workers with a history of exposure to vinyl chloride. An increase in fetal mortality has been reported among wives of workers who had been exposed to vinyl chloride.

• Signs and symptoms of exposure
1. *Short-term (acute):* Exposure to vinyl chloride can cause dizziness, light-headedness, nausea, dullness of visual and auditory responses, drowsiness, and unconsciousness. Irritation of the skin and eyes can also occur. Skin contact with the liquid can cause frostbite.
2. *Long-term (chronic):* Exposure to vinyl chloride can cause thickening of the skin, contact and allergic dermatitis, fatigue, coughing and sneezing, abdominal pain, gastrointestinal bleeding, nausea, vomiting, indigestion, diarrhea, jaundice, weight loss, anorexia, and a cold and tingling sensation of the hands and feet.

RECOMMENDED MEDICAL PRACTICES

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

A medical surveillance program should include systematic collection and epidemiologic analysis of 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 the 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 vinyl chloride, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin, liver, kidneys, and cardiovascular, 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).

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 vinyl chloride. 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 serological tests of liver function and markers for infection with Hepatitis B virus.

• 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 vinyl chloride. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, kidneys, and cardiovascular, 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 test should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and ATS: standardized questionnaires and test 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 vinyl chloride 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: Liver cancer (hemangiosarcoma) and "white finger" (Raynaud's syndrome, secondary to vasculitis)

MONITORING AND MEASUREMENT PROCEDURES

• Method

Sampling and analysis may be performed by collecting vinyl chloride vapors with tandem charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure vinyl chloride may also be used if available. A detailed sampling and analytical method for vinyl chloride may be found in the *NIOSH Manual of Analytical Methods* (method number 1007).

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 vinyl chloride.

SANITATION

Clothing which is contaminated with vinyl chloride 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 vinyl chloride from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of vinyl chloride'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 vinyl chloride should be promptly washed with soap and water.

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

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

COMMON OPERATIONS AND CONTROLS

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

Table 2.—Operations and methods of control for vinyl chloride

Operations	Controls
During the manufacture of monomer, polymer, copolymer, and terpolymer	Process enclosure, personal protective equipment
During the transfer of monomer to tank cars or polymerization reactors; during maintenance work on tanks or reactors	Local exhaust ventilation, personal protective equipment
During the cleaning of polymerization reaction tanks	Process enclosure, 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 vinyl chloride, an eye-wash fountain should be

provided within the immediate work area for emergency use.

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

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

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

1. 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.

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 vinyl chloride

Condition	Minimum respiratory protection*
Any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode
Planned or emergency entry into environments containing unknown or any detectable concentration	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
	Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in 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 canister providing protection against the compound of concern
	Any appropriate escape-type self-contained breathing apparatus

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

* U.S. GOVERNMENT PRINTING OFFICE:1993-750-004/80503

Occupational Health Guideline for Vinyl Toluene

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: $CH_3C_6H_4CH=CH_2$
- Synonyms: Methylstyrene; tolylethylene; meta- and para-vinyltoluene (mixed isomers)
- Appearance and odor: Colorless liquid with a strong, disagreeable odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for vinyl toluene is 100 parts of vinyl toluene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 480 milligrams of vinyl toluene 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 vinyl toluene from 100 ppm to 50 ppm.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Vinyl toluene 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: Vinyl toluene may cause irritation of the nose, throat, eyes, and skin. It may also cause drowsiness.

2. Long-term Exposure: Repeated exposure 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 vinyl toluene.

- **Recommended medical surveillance**

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

—Kidney disease: Although vinyl toluene 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 vinyl toluene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Liver disease: Although vinyl toluene 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: Vinyl toluene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

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

- **Summary of toxicology**

The main toxic effect of vinyl toluene is irritation of the eyes, upper respiratory tract, and skin. With prolonged and repeated contact and absorption of high doses, 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.

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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: 118
  2. Boiling point (760 mm Hg): 168 C (334 F)
  3. Specific gravity (water = 1): 0.92
  4. Vapor density (air = 1 at boiling point of vinyl toluene): 4.1
  5. Melting point: −77 C (−106 F)
  6. Vapor pressure at 20 C (68 F): 1.1 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): 0.009
  8. Evaporation rate (butyl acetate = 1): Less than 0.5
- **Reactivity**
  1. Conditions contributing to instability: Vinyl toluene is stabilized by a polymerization inhibitor (10 to 50 ppm of tert-butylcatechol). If this is not present in adequate concentrations, vinyl toluene can polymerize and explode in the container.
  2. Incompatibilities: Contact with oxidizing agents may cause fires and explosions. Also, catalysts for vinyl polymerization, such as peroxides, strong acids, and aluminum chloride should be avoided.
  3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving vinyl toluene.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 53 C (127 F) (closed cup)
  2. Autoignition temperature: 495 C (923 F)
  3. Flammable limits in air, % by volume: Lower: 0.1; Upper: 11
  4. Extinguishant: Dry chemical, carbon dioxide, or foam.
- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold of vinyl toluene.
  2. Irritation Levels: According to the ILO, vinyl toluene "gives rise to irritation of the nasal and conjunctival mucosae at 400 ppm and is detectable at 50 ppm."
  3. Evaluation of Warning Properties: Since the ILO reports that vinyl toluene is detectable at a concentration below the permissible exposure limit, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

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

SANITATION

• Skin that becomes contaminated with liquid vinyl toluene should be promptly washed or showered with soap or mild detergent and water to remove any vinyl toluene.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Use during spray applications of vinyl toluene polyester surface coatings	Local downdraft ventilation; personal protective equipment
Liberation during preparation of unsaturated polyester resins and alkyd coatings	Local downdraft ventilation
Use during application of specialty paints and varnishes	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of thermoplastic moldings via extrusion, injection, stamping, or other processes	Local downdraft 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 vinyl toluene 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 vinyl toluene gets on the skin, promptly flush the contaminated skin with water. If vinyl toluene 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 vinyl toluene, 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 vinyl toluene 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 vinyl toluene 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. Vinyl toluene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal methods:

Vinyl toluene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a flammable liquid.

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RESPIRATORY PROTECTION FOR VINYL TOLUENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
400 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).
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.

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

Occupational Health Guideline for Warfarin

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: $C_{19}H_{16}O_4$
- Synonyms: 3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin; WARF compound; compound 42; coumadin
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for warfarin is 0.1 milligram of warfarin per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Warfarin 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 exposure to warfarin may cause bleeding difficulties by impairing the clotting ability of the blood. Problems which may occur include easy bruising, nose bleeds, vomiting blood, bloody or tar-like stools, and bloody urine. A single large dose has been reported to be capable of causing bleeding problems after several days' delay.

- **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 warfarin.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to warfarin 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 blood disorders with bleeding tendencies would be expected to be at increased risk from exposure. Examination of the blood should be stressed.

—A complete blood count: Warfarin has been shown to cause hypoprothrombinemia in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Prothrombin time: Warfarin has been shown to cause hypoprothrombinemia in humans. A quick 1-stage prothrombin time or a thrombotest should be performed.

—Urinalysis: Warfarin has been shown to cause an increased bleeding tendency. A urinalysis should be obtained with emphasis on examination for red blood cells as an early indicator of internal bleeding.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Warfarin as the dust or in solution causes hypoprothrombinemia and vascular injury which results in internal hemorrhage. It suppresses the hepatic formation of prothrombin and of factors VII, IX, and X, causing a markedly reduced prothrombin activity of the blood; it also causes dilation and engorgement of blood vessels and an increase in capillary fragility. The inhibition of prothrombin formation does not become apparent until the prothrombin reserves are depleted, which usually requires exposure for a number of days. A single large

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 may cause intoxication after a latency period of several days, but in a series of acute ingestion episodes there were no signs of hemorrhage or depression of plasma prothrombin. A farmer whose hands were intermittently wetted with a 0.5% solution of warfarin over a period of 24 days developed gross hematuria 2 days after the last contact with the solution; the following day, spontaneous hematomas appeared on the arms and legs. Within 4 days, there was also epistaxis, punctate hemorrhages of the palate and mouth, and bleeding from the lower lip. The bleeding time was over 30 minutes; the clotting time, 11 minutes, 30 seconds; prothrombin index, 17; and the prothrombin percentage (thrombotest), 5. Four days later, after treatment for 2 days with phytonadione, the values were in the normal range. Other effects of warfarin intoxication have included back pain, abdominal pain, vomiting, melena, and petechiae of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 308.3
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): Greater than 1
  4. Vapor density (air = 1 at boiling point of warfarin): Not applicable
  5. Melting point: 161 C (322 F)
  6. Vapor pressure at 20 C (68 F): Data not available
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): 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 carbon monoxide) may be released in a fire involving warfarin.
  4. Special precautions: None.
- **Flammability**
  1. Flash point: Not applicable
  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**

Warfarin is not known to be an eye irritant. It has produced hemorrhages in the retina, however, through its systemic toxicity (Grant).

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 warfarin 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 warfarin or liquids containing warfarin.
- If employees' clothing has had any possibility of being contaminated with warfarin or liquids containing warfarin, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with warfarin should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of warfarin from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the warfarin, the person performing the operation should be informed of warfarin's hazardous properties.
- Non-impervious clothing which becomes contaminated with warfarin should be removed promptly and not reworn until the warfarin is removed from the clothing.

SANITATION

• Skin that becomes contaminated with warfarin should be promptly washed or showered with soap or mild detergent and water to remove any warfarin.
• Eating and smoking should not be permitted in areas where warfarin or liquids containing warfarin are handled, processed, or stored.
• Employees who handle warfarin or liquids containing warfarin 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 warfarin may occur and control methods which may be effective in each case:

Operation	Controls
Application as a rodenticide	General dilution ventilation; personal protective equipment
Formulation of rodenticides	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Manufacture of warfarin	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 warfarin dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
• **Skin Exposure**
If warfarin or liquids containing warfarin get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If warfarin or liquids containing warfarin penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. Get medical attention promptly.
• **Breathing**
If a person breathes in large amounts of warfarin, 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 warfarin 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 warfarin 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:
Warfarin may be disposed of:
1. By making packages of warfarin in paper or other flammable material and burning in a suitable combustion chamber.
2. By dissolving warfarin in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR WARFARIN

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
0.5 mg/m³ or less	Any dust respirator, except single-use.
1 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.
5 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

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

Occupational Health Guideline for Xylene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_4(CH_3)_2$
- Synonyms: Commercial xylene (xylol) is a mixture, mostly the meta-isomer. 1) O-xylene, ortho-xylene, 1,2-dimethylbenzene; 2) m-xylene, meta-xylene, 1,3-dimethylbenzene; 3) p-xylene, para-xylene, 1,4-dimethylbenzene
- Appearance and odor: Colorless liquids with aromatic odors (pure p-xylene is a solid below 12.7 C (55 F)).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for xylene is 100 parts of xylene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 435 milligrams of xylene per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 100 ppm averaged over a work shift of up to ten hours per day, forty hours per week, with an acceptable ceiling level of 200 ppm averaged over a 10-minute period. The NIOSH Criteria Document for Xylene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Xylene 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: Xylene vapor may cause irritation of the eyes, nose, and throat. At high concentrations, xylene vapor may cause severe breathing difficulties which may be delayed in onset. At high concentrations, it may also cause dizziness, staggering, drowsiness, and unconsciousness. In addition, breathing high concentrations may cause loss of appetite, nausea, vomiting, and abdominal pain. Liquid xylene may be irritating to the eyes and skin. Exposure to high concentrations of xylene vapor may cause reversible damage to the kidneys and liver.

2. Long-term Exposure: Repeated or prolonged exposure to xylene may cause a skin rash. Repeated exposure of the eyes to high concentrations of xylene vapor may cause reversible eye 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 xylene.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to xylene 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, eyes, gastrointestinal tract, blood, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Xylene has been shown to cause reversible hematopoietic depression 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.

—Liver function tests: Since liver damage has been observed in humans exposed to xylene, a profile of liver

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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function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has been observed in humans exposed to xylene, 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 biannual basis.

• **Summary of toxicology**

Xylene vapor irritates the eyes, mucous membranes, and skin; at high concentrations it causes narcosis. In animals, xylene causes blood changes reflecting mild toxicity to the hematopoietic system. Repeated exposure of rabbits to 1150 ppm of a mixture of isomers of xylene for 40 to 55 days caused a reversible decrease in red and white cell count and an increase in thrombocytes; exposure to 690 ppm for the same time period caused only a slight decrease in the white cell count. Three painters working in a confined space of a fuel tank were overcome by xylene vapors estimated to be 10,000 ppm; they were not found until 18.5 hours after entering the tank, and one died from pulmonary edema shortly thereafter; the other two recovered completely in 2 days; both had temporary hepatic impairment (inferred from elevated serum transaminase levels) and one of them had evidence of temporary renal impairment (increased blood urea and reduced creatinine clearance). In humans, exposure to undetermined but high concentrations caused dizziness, excitement, drowsiness, incoordination and a staggering gait. Workers exposed to concentrations above 200 ppm complain of anorexia, nausea, vomiting, and abdominal pain. Brief exposure of humans to 200 ppm caused irritation of the eyes, nose, and throat. There are reports of reversible corneal vacuolation in workers exposed to xylene, or to xylene plus other volatile solvents. The liquid is a skin irritant and causes erythema, dryness, and defatting; prolonged contact may cause the formation of vesicles.

CHEMICAL AND PHYSICAL PROPERTIES

Data in the following section are presented for xylene's three isomers: 1) ortho, 2) meta, and 3) para.

• **Physical data**

1. Molecular weight: 106.2

2. Boiling point (760 mm Hg): 1) 144.4 C (292 F); 2) 138.9 C (282 F); 3) 138.3 C (281 F)

3. Specific gravity (water = 1): 1) 0.88; 2) 0.86; 3) 0.86

4. Vapor density (air = 1 at boiling point of xylene): 3.7

5. Melting point: 1) −25 C (−12 F); 2) −48 C (−54 F); 3) 13 C (55 F)

6. Vapor pressure at 20 C (68 F): 1) 7 mm Hg; 2) 9 mm Hg; 3) 9 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 1) 0.00003; 2) 0.00003; 3) 0.00003

8. Evaporation rate (butyl acetate = 1): 1) 0.7; 2) 0.7; 3) 0.7

• **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 xylene.

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

• **Flammability**

1. Flash point: 1) 32 C (90 F) (closed cup); 2) 28.9 C (84 F); 3) 27.2 C (81 F)

2. Autoignition temperature: 1) 465 C (869 F); 2) 530 C (986 F); 3) 530 C (986 F)

3. Flammable limits in air, % by volume: Lower: 1) 1.0; 2) 1.1; 3) 1.1; Upper: 1) 6.0; 2) 7.0; 3) 7.0

4. Extinguishant: Foam, carbon dioxide, dry chemical

• **Warning properties**

1. Odor Threshold: Patty states that "the initial odor of 200 ppm has an intensity of approximately 3 and an irritation value of 1. As in most other instances, olfactory fatigue occurs rapidly and the odor is no longer detected at this concentration."

2. Eye Irritation Level: The AIHA *Hygienic Guide* states that "exposure to vapors at 200 ppm caused eye irritation in most of the persons tested. Lesions in the form of fine vacuoles in the cornea of cats exposed to commercial xylene vapors have been observed."

3. Other Information: The *Handbook of Industrial Organic Chemicals* states that xylene "may be irritating to eyes, nose and throat as exposure exceeds threshold limit." The *Hygienic Guide* notes that 200 ppm causes irritation of the nose and throat.

4. Evaluation of Warning Properties: Through its irritant effects, xylene can be detected within three times the permissible exposure limit. For the purposes of this guideline, therefore, xylene 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 xylene. Each measurement

should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of 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 xylene may be used. An analytical method for xylene 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 or solid xylene.

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

• Any clothing which becomes wet with liquid xylene should be removed immediately and non-impervious clothing which becomes contaminated with xylene should be removed promptly and not reworn until the xylene is removed from the clothing.

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

SANITATION

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

• Employees who handle liquid or solid xylene 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 xylene may occur and control methods which may be effective in each case:

Operation	Controls
Use as an intermediate during manufacture of plastics, synthetic fibers, and mixed/pure isomers	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use as diluent or solvent in surface coatings, printing operations, and manufacture of rubber; degreasing agent in plastics and electronics manufacture; in organic synthesis reactions and manufacture of epoxy resins	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in formulation of insecticides	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment
Use in manufacture of xylene-formaldehyde resins; pharmaceuticals, vitamins, leather; and as a sterilizing agent for cat-gut and in microscopy	Process enclosure; local exhaust ventilation; general mechanical ventilation; personal protective equipment

Operation	Controls
Use during blending of motor and aviation fuels	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 or solid xylene 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 or solid xylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid or solid xylene penetrates 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 xylene, 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 xylene 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 xylene 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. Xylene 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 xylene vapors are permitted.
4. If the solid form, allow to melt and treat as in (3) above.

• Waste disposal method:

Xylene may be disposed of by atomizing in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR XYLENE (XYLOL)

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 Xylidine

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: $(CH_3)_2C_6H_3NH_2$
- Synonyms: 2,4-Dimethylaniline, etc. (6 isomers); xylidine isomers; xylidines mixed o-m-p
- Appearance and odor: Pale yellow to brown liquid with a weak, aromatic amine odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for xylidine is 5 parts of xylidine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 25 milligrams of xylidine 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 xylidine from 5 ppm to 2 ppm with a skin notation.

- Method

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Xylidine 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 xylidine may affect the ability of the blood to carry oxygen normally. The earliest effect may be a bluish discoloration 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. Heart, liver, and kidney damage have occurred in animals exposed to this chemical, but have not been reported in man.

- **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 xylidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to xylidine 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, lungs, liver, kidneys, and cardiovascular system should be stressed.

—A complete blood count: Xylidine has been shown to cause methemoglobinemia. 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.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin concentration in blood should be determined when xylidine intoxication is suspected.

- **Summary of toxicology**

Xylidine absorption, whether from inhalation of the vapor or absorption of the liquid through skin, causes anoxia due to the formation of methemoglobin; lung, liver, and kidney damage results in experimental animals. Repeated exposure of cats to 138 ppm caused loss of leg coordination, cyanosis, prostration, and death; at autopsy there was pulmonary edema and lobular pneumonia, necrosis of the liver, and toxic nephrosis. In cats exposed to 132 ppm for 3 days the methemoglobin concentration was 55%; repeated exposure of cats to

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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17.4 ppm caused toxic hepatitis and some deaths, while repeated exposure to 7.8 ppm caused no adverse effects. Liquid xylidine penetrated the skin of rabbits in sufficient quantity to cause cyanosis and death; there were no local effects on the skin. In humans, the onset of xylidine intoxication may be insidious, in that early warning signs of methemoglobinemia such as headache and dizziness are not always interpreted as being due to overexposure, and even mild cyanosis may not be recognized.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 121.2
2. Boiling point (760 mm Hg): 212– 226 C (415–439 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of xylidine): 4.17
5. Melting point: Data not available
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): Data not available

- **Reactivity**

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

- **Flammability**

1. Flash point: 96.7 C (206 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 1.5 (calculated at flash point)
4. Extinguishant: Carbon dioxide, dry chemical, foam

- **Warning properties**

1. Odor Threshold: May reports an odor threshold of 0.0048 ppm.
2. Eye Irritation Level: Xylidine is not known to be an eye irritant.
3. Evaluation of Warning Properties: Since the odor threshold of xylidine is below the permissible exposure limit, xylidine 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 xylidine in an adsorption tube containing silica gel, followed by desorption with ethanol, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure xylidine may be used. An analytical method for xylidine 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).
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- 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 xylidine.
- Clothing contaminated with xylidine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of xylidine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the xylidine, the person performing the operation should be informed of xylidine's hazardous properties.
- Where exposure of an employee's body to liquid xylidine may occur, facilities for quick drenching of the

RESPIRATORY PROTECTION FOR XYLENE (XYLOL)

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.

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- Appearance and odor: Pale yellow to brown liquid with a weak, aromatic amine odor.

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- **Method**

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Xylidine 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 xylidine may affect the ability of the blood to carry oxygen normally. The earliest effect may be a bluish discoloration 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. Heart, liver, and kidney damage have occurred in animals exposed to this chemical, but have not been reported in man.

- **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 xylidine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to xylidine 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, lungs, liver, kidneys, and cardiovascular system should be stressed.

—A complete blood count: Xylidine has been shown to cause methemoglobinemia. 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.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin concentration in blood should be determined when xylidine intoxication is suspected.

- **Summary of toxicology**

Xylidine absorption, whether from inhalation of the vapor or absorption of the liquid through skin, causes anoxia due to the formation of methemoglobin; lung, liver, and kidney damage results in experimental animals. Repeated exposure of cats to 138 ppm caused loss of leg coordination, cyanosis, prostration, and death; at autopsy there was pulmonary edema and lobular pneumonia, necrosis of the liver, and toxic nephrosis. In cats exposed to 132 ppm for 3 days the methemoglobin concentration was 55%; repeated exposure of cats to

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Occupational Health Guideline for Yttrium and Compounds (as Yttrium)

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 yttrium and compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Yttrium metal

- Formula: Y
- Synonyms: None
- Appearance and odor: Odorless, silvery solid.

Yttrium nitrate hexahydrate

- Formula: $Y(NO_3)_3 \cdot 6H_2O$
- Synonyms: None
- Appearance and odor: Colorless to pink, odorless solid.

Yttrium chloride

- Formula: YCl_3
- Synonyms: None
- Appearance and odor: Colorless, odorless solid.

Yttrium oxide

- Formula: Y_2O_3
- Synonyms: None
- Appearance and odor: Colorless, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Animal experiments suggest that yttrium and compounds can affect the body if they are inhaled or if they come in contact with the eyes. These experiments also suggest that they can also affect the body if they are swallowed.

- **Effects of overexposure**

Long-term exposure: Yttrium chloride particles which have become embedded in the eye have caused chemical eye damage in humans. Animal studies have shown the yttrium and compounds have caused irritation of the lungs, lung damage, 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 yttrium and compounds.

- **Recommended medical surveillance**

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

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

—Eye disease: Yttrium may cause severe eye damage. Those with pre-existing eye problems may be at increased risk from exposure.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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

• **Summary of toxicology**

Yttrium and compounds have caused pulmonary irritation in animals. Systemic absorption of the citrate complex of yttrium by animals resulted in dyspnea and pulmonary edema; yttrium chloride produced liver edema, portal congestion, pleural effusion, and pulmonary hyperemia. Intraperitoneal injection of yttrium chloride in animals caused peritonitis with serous or hemorrhagic ascites. Intratracheal injection of 50 mg of yttrium oxide in rats produced diffuse sclerosis of the lungs. Application of a 0.1 M solution of yttrium chloride to the eyes of rabbits caused no injury; similar exposure of eyes from which the corneal epithelium had been removed resulted in immediate slight haziness of the cornea which subsequently became opaque and vascularized.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Yttrium metal**

1. Molecular weight: 88.9
2. Boiling point (760 mm Hg): 2927 C (5300 F)
3. Specific gravity (water = 1): 4.47
4. Vapor density (air = 1 at boiling point of yttrium metal): Not applicable
5. Melting point: 1509 C (2748 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—Yttrium nitrate hexahydrate**

1. Molecular weight: 383
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 2.68
4. Vapor density (air = 1 at boiling point of yttrium nitrate hexahydrate): Not applicable
5. Melting point: 100 C (212 F) (loses water)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 142
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Yttrium chloride**

1. Molecular weight: 195.3
2. Boiling point (760 mm Hg): 1510 C (2750 F)
3. Specific gravity (water = 1): 2.67
4. Vapor density (air = 1 at boiling point of yttrium chloride): Not applicable
5. Melting point: 720 C (1328 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 79
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Yttrium oxide**

1. Molecular weight: 225.8
2. Boiling point (760 mm Hg): 4300 C (7772 F)
3. Specific gravity (water = 1): 4.84
4. Vapor density (air = 1 at boiling point of yttrium oxide): Not applicable
5. Melting point: 2416 C (4380 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of yttrium nitrate with combustible materials may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released when yttrium nitrate decomposes.
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: Not applicable

• **Warning properties**

Yttrium 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 on a cellulose membrane filter followed by treatment with nitric and perchloric acids, solution in hydrochloric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for yttrium and 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. How-

ever, 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 dust- and splash-proof safety goggles to prevent any possibility of eye contact with yttrium nitrate hexahydrate, yttrium chloride, yttrium oxide, or liquids containing these compounds.

• Where there is any possibility that employees' eyes may be exposed to yttrium nitrate hexahydrate, yttrium chloride, yttrium oxide, or liquids containing these compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during purification; and during manufacture of alloys	Local exhaust ventilation; personal protective equipment
Use in manufacture of red phosphorus used in color TV picture tubes; fluorescent and mercury vapor lamps	Local exhaust ventilation; personal protective equipment
Use in manufacture of yttrium-iron-garnet (YIG) and YAG (aluminum) for use as electronic components in telephones, radar and space communications networks; and as simulated diamonds	Local exhaust ventilation; personal protective equipment
Use in manufacture of ceramics for use in high temperature furnaces and high intensity incandescent lamps	Local exhaust ventilation; personal protective equipment
Use in manufacture of refractories for stable, high temperature, high strength composition	Local exhaust ventilation; personal protective equipment
Use in manufacture of lasers	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 yttrium and 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 yttrium and compounds get on the skin, wash the contaminated 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 yttrium or yttrium 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 yttrium and 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 yttrium and 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 yttrium and compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Yttrium and compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

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RESPIRATORY PROTECTION FOR YTTRIUM AND COMPOUNDS (AS YTTRIUM)

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.
500 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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

Occupational Health Guideline for Zinc Chloride 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: $ZnCl_2$
- Synonyms: None
- Appearance and odor: White fume with an acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Zinc chloride 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: Exposure to zinc chloride fume may cause shortness of breath, a feeling of constriction in the chest, abdominal pain, watering of the eyes, burning of the eyes and throat, and coughing with phlegm and bloody sputum. It may also cause a blue color of the skin and lips. In addition, it may cause pneumonia. Breathing difficulties may not appear for several hours after exposure has ceased. Fatal exposures have occurred.

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 zinc chloride fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to zinc chloride 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. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Zinc chloride fume causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Zinc chloride fume 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. Determination of zinc in the urine may be helpful in evaluating the extent of absorption.

- **Summary of toxicology**

Zinc chloride fume irritates the eyes, mucous membranes, and skin, and causes delayed pulmonary edema. Ten deaths and 25 cases of non-fatal injury occurred among 70 persons exposed to a high concentration of zinc chloride released from smoke generators; presenting symptoms were conjunctivitis (two with burns of the corneas), irritation of nose and throat, cough with copious sputum, dyspnea, constrictive sensation in the chest, stridor, retrosternal pain, nausea, epigastric pain, and pale gray cyanosis. Of the 10 fatalities, a few died immediately or in a few hours from pulmonary edema, while those who survived longer developed bronchopneumonia. Between the second and fourth days after exposure, almost all cases developed moist, adventitious sounds in the lungs, and the majority continued to

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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present a pale cyanotic color; a prominent feature was the disparity between the severe symptoms and the paucity of physical signs in the lungs; recovery occurred within 1 to 6 weeks after the incident. A firefighter was fatally exposed to a high but undetermined concentration of zinc chloride fume from a smoke generator; on admission to the hospital, the patient complained of nausea, sore throat, and chest tightness aggravated by deep inspiration. He initially improved but then developed tachypnea, substernal soreness, fever, cyanosis, and coma; the lung fields were clear on auscultation despite diffuse pulmonary infiltrations seen on the chest roentgenogram; death occurred 18 days after exposure, and autopsy revealed active fibroblastic proliferation and cor pulmonale. Injection of zinc chloride solution into the testes of 49 Syrian hamsters resulted in areas of necrosis occupying about 25% of each testis; two embryonal carcinomata of the testis were found 10 weeks later at necropsy.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 136.3
  2. Boiling point (760 mm Hg): 732 C (1350 F) (for solid)
  3. Specific gravity (water = 1): 2.91 (solid)
  4. Vapor density (air = 1 at boiling point of zinc chloride fume): Not applicable
  5. Melting point: 283 C (541 F) (for solid)
  6. Vapor pressure at 20 C (68 F): Not applicable
  7. Solubility in water, g/100 g water at 25 C (77 F): 81
  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**

Grant states that "dilute solutions (0.2% to 1%) have long been used as astringent eye drops without difficulty, but concentrated solutions and pastes such as encountered industrially have caused very severe injuries of the cornea in numerous cases of accidental splash in the eye. . . . Guillery found that applying 10% zinc chloride solution for 4 to 5 minutes to a rabbit's eye caused loss of corneal endothelium and extensive infiltration." No information is available concerning the effects on the eye specifically of the fume of zinc chloride.

The *Documentation of TLV's* reports, "Elkins stated that zinc chloride is an irritant . . . . Ferry, in investigating a borderline condition, found that levels between 0.07 and 0.4 mg/m^3 for 30 minutes did not result in sensory effects. The fume is corrosive to metals at these levels, 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**

At the time of publication of this guideline, no measurement method for zinc chloride fume 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 zinc chloride fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fluxing iron/steel prior to galvanizing	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from arc welding of galvanized iron and steel pipes	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from fluxing agent in some solder composition	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from vulcanizing and reclaiming processes for rubber	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from solutions in glass and metal etching	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from manufacture of dry cell batteries	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation from petroleum refining operations	Process enclosure; 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.

- **Breathing**

If a person breathes in large amounts of zinc chloride 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.

LEAK 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 zinc chloride fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Zinc Chloride Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Milliken, J. A., et al.: "Acute Interstitial Pulmonary Fibrosis Caused by a Smoke Bomb," *Canadian Medical Association Journal*, 88:36-39, 1963.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Vallee, B. L.: "Zinc and Its Biological Significance," *A.M.A. Archives of Industrial Health*, 16:147-154, 1957.

RESPIRATORY PROTECTION FOR ZINC CHLORIDE FUME

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
10 mg/m³ or less	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 full facepiece and a high efficiency particulate filter.
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.
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 Zinc 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: ZnO
- Synonyms: None
- Appearance: White fume.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for zinc oxide fume is 5 milligrams of zinc oxide fume 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 5 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 15 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Zinc Oxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Zinc oxide fume can affect the body if it is inhaled.

- **Effects of overexposure**

1. Short-term Exposure: Zinc oxide fume causes a flu-like illness called metal fume fever. Symptoms of metal fume fever include headache, fever, chills, muscle aches, nausea, vomiting, weakness, and tiredness. The symptoms usually start several hours after exposure. The attack may last 6 to 24 hours. Metal fume fever is more likely to occur after a period away from the job (after weekends or vacations). High levels of exposure to zinc oxide fume may cause a metallic or sweet taste in the mouth, dryness and irritation of the throat, and coughing at the time of exposure.

2. Long-term Exposure: None known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to zinc oxide fume.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to zinc 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: Zinc oxide fume may cause respiratory impairment. Persons with pulmonary disease may be more susceptible to the effect os zinc oxide fume. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Persons with pre-existing pulmonary disease may be more susceptible to the effects of zinc oxide fume. 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. Determination of zinc in the urine may be helpful in evaluating the extent of absorption.

- **Summary of toxicology**

Inhalation of zinc oxide fume causes an influenza-like illness termed metal fume fever. Heavy human exposure to zinc oxide fume may cause an immediate dryness and irritation of the throat, a sweet or metallic taste followed by substernal tightness and constriction in the chest, and a dry cough. Several hours following exposure the subject develops fever, lassitude, malaise, fatigue, frontal headache, low back pain, muscle cramps, and occasionally blurred vision, nausea, and vomiting.

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
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National Institute for Occupational Safety and Health

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

September 1978

Physical examination reveals fever, eventually followed by perspiration and chills, dyspnea, rales throughout the chest, and tachycardia; in some instances there has been a reversible reduction in pulmonary vital capacity; there is usually leukocytosis, which may amount to 12,000 to 16,000/MM3. An attack usually subsides after 6 to 12 hours but may last for up to 24 hours; recovery is usually complete. Most workers rapidly develop an immunity to these attacks, but it is as quickly lost; attacks tend to be more severe on the first day of the work-week. Only freshly formed fume causes the illness, presumably because flocculation occurs in the air; the larger particles that form are deposited in the upper respiratory tract and do not penetrate deeply into the lungs. Chills have been reported in workers from exposure to concentrations of zinc oxide fume below 5 mg/m^3.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 81.37
  2. Boiling point (760 mm Hg): Solid sublimes
  3. Specific gravity (water = 1): 5.6 (solid)
  4. Vapor density (air = 1 at boiling point of zinc oxide fume): Not applicable
  5. Melting point: Greater than 1800 C (greater than 3272 F)
  6. Vapor pressure at 20 C (68 F): Not applicable
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble (solid)
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Zinc oxide fume may react violently with chlorinated rubber.
  3. Hazardous decomposiiton products: None
  4. Special precautions: None
- **Flammability**
  1. Not combustible
- **Warning properties**

Zinc oxide fume is not known to be an eye irritant.

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 zinc oxide fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of zinc oxide on a cellulose membrane filter, followed by solublizing the zinc with nitric acid and analyzing by atomic absorption spectrophotometry. An analytical method for zinc 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 zinc oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during brazing, welding, burning, and cutting of zinc and galvanized metals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from founding of brass, copper, and zinc, and galvanizing of iron and steel	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from abrasive cleaning of galvanized metal surface	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberating during use as a ceramic flux	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation during recovery of impure lead blast furnace slag; from manufacture of glass to increase brilliance and luster of glass	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from use as an intermediate in manufacture of other zinc compounds; in manufacture of electronic devices	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation from use as a filler material in crushed stone industry	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 zinc 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.

LEAK 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 zinc oxide fume are inadvertently released, ventilate the area of the release to disperse the fume.

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RESPIRATORY PROTECTION FOR ZINC OXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate 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.
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 Zirconium Compounds (as Zirconium)

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 zirconium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Zirconium oxide

- Formula: ZrO_2
- Synonyms: Zirconia
- Appearance and odor: Colorless, odorless solid.

Zirconium oxychloride

- Formula: $ZrOCl_2\ 8H_2O$
- Synonyms: Zirconyl chloride octahydrate
- Appearance and odor: Colorless, odorless solid.

Zirconium tetrachloride

- Formula: $ZrCl_4$
- Synonyms: ZC-4
- Appearance and odor: Colorless solid with an acrid odor in moist air.

Zirconium hydride

- Formula: ZrH_2
- Synonyms: Zirconium dihydride
- Appearance and odor: Odorless, metallic powder.

Zirconyl acetate

- Formula: $H_2ZrO_2(C_2H_3O_2)_2$
- Synonyms: Diacetatozirconic acid
- Appearance: Colorless solid.
- **Summary of toxicology**

PERMISSIBLE EXPOSURE LIMIT (PEL)

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

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Zirconium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin.

- **Effects of overexposure**

Skin rash has been reported from exposure to zirconium-containing deodorants.

- **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 zirconium compounds.

- **Recommended medical surveillance**

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

—Chronic respiratory disease: Zirconium compounds (silicate) have been reported to cause radiographic changes in animals due to pulmonary retention. Zirconium hexachloride may be irritating to the mucous membranes of the respiratory tract.

—Skin disease: Zirconium may cause granulomas of the skin. 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.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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

September 1978

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

• **Summary of toxicology**

Zirconium compounds are of generally low toxicity, although granulomata have been produced by repeated topical applications of zirconium salts to human skin. In rats, the oral LD50 of several zirconium compounds ranged from 2.5 to 10 g/kg. Repeated inhalation of zirconium tetrachloride mist by dogs for 2 months at 6 mg/m³ as zirconium caused slight decreases in hemoglobin and in erythrocyte counts, with some increases in mortality over that of controls; these effects may have been due to the liberation of hydrogen chloride. However, animals exposed to zirconium dioxide dust for 1 month at 75 mg/m³ as zirconium showed no detectable effects. Rats exposed to high concentrations of zirconium silicate dust for 7 months developed radiographic shadows in the lungs; these were attributed solely to the deposition of the radiopaque particles, since histologic examination showed no cellular reaction. A study of 22 workers exposed to fumes from a zirconium reduction process for 1 to 5 years revealed no abnormalities referable to the exposure. There are no well-documented cases of toxic effects from industrial exposure. Granulomata of the human axillary skin have occurred from use of deodorants containing zirconium, although the metal is not regarded as a skin sensitizer in other types of exposure.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Zirconium oxide**

1. Molecular weight: 123.2
2. Boiling point (760 mm Hg): 5000 C (9032 F)
3. Specific gravity (water = 1): 5.8 to 6.2
4. Vapor density (air = 1 at boiling point of zirconium oxide): Not applicable
5. Melting point: 2700 C (4892 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—Zirconium oxychloride**

1. Molecular weight: 322.3
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of zirconium oxychloride): Not applicable
5. Melting point: 110 C (230 F) (approximately)
6. Vapor pressure at 20 C (68 F): 9 to 13 mm Hg vapor pressure of water
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Zirconium tetrachloride**

1. Molecular weight: 233
2. Boiling point (760 mm Hg): 331 C (628 F) (sublimes)
3. Specific gravity (water = 1): 2.8
4. Vapor density (air = 1 at boiling point of zirconium tetrachloride): Not applicable
5. Melting point: 331 C (628 F) (sublimes)
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—Zirconium hydride**

1. Molecular weight: 93.2
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 5.7
4. Vapor density (air = 1 at boiling point of zirconium hydride): Not applicable
5. Melting point: Decomposes above 300 C (572 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 low
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Zirconyl acetate**

1. Molecular weight: Very high (a polymer)
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of zirconyl acetate): Not applicable
5. Melting point: Data not available
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: Zirconium tetrachloride will decompose in the presence of moist air. Elevated temperatures (greater than 315 C (600 F)) cause zirconium hydride to decompose to give off flammable hydrogen gas.
2. Incompatibilities: Zirconium tetrachloride reacts with water or with moisture in air to form hydrochloric acid fume. Contact with alkali metals such as sodium or potassium may cause explosions. Contact of zirconium hydride with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving zirconium compounds.
4. Special precautions: Zirconium tetrachloride will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For zirconium hydride: 270 C (518 F); for others: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For zirconium hydride, sand or

inert powder; for others, not applicable

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 zirconium compounds on a filter, followed by treatment with nitric and perchloric acids, solution in acid, and atomic absorption spectrophotometric analysis. An analytical method for zirconium compounds is in the *NIOSH Manual of Analytical Methods,* 2nd Ed., Vol. 3, 1977, and Vol. 4, 1978, 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 zirconium oxide, zirconium oxychloride, zirconyl acetate, or liquids containing these compounds, and to prevent skin contact with zirconium tetrachloride or liquids containing zirconium tetrachloride, where skin contact may occur.

• If employees' clothing may have become contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.

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

• Where exposure of an employee's body to zirconium tetrachloride or liquids containing zirconium tetrachloride 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 zirconium oxide, zirconium oxychloride, zirconyl acetate or zirconium tetrachloride 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 zirconium tetrachloride or liquids containing zirconium tetrachloride contacting the eyes.

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

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

SANITATION

• Skin that becomes contaminated with zirconium oxide, zirconium oxychloride, zirconyl acetate, or zirconium tetrachloride should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.

• Employees who handle zirconium oxide, zirconium oxychloride, zirconyl acetate, zirconium tetrachloride, or liquids containing these 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 zirconium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from refining and casting operations, dies for metal extrusion and spout linings for continuous casting; during preparation of alloys; during manufacture of metal or alloys in nuclear power, aerospace, and chemical industries	Process enclosure; local exhaust ventilation; general dilution ventilation
Use in manufacture of ceramics, glass, and porcelains; synthesis of pigments, dyes, and water repellants; use in tanning operations	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as abrasive and polishing materials; use as an igniter in manufacture of munitions and other items as detonators, photoflash bulbs, and lighter flints; use in manufacture of skin ointments and antiperspirants	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as a gas getter in manufacture of high vacuum tubes and radio valves; use as a deoxidizer, denitrifier, and desulfurizer in iron and steel manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation
Liberation from chemical synthesis	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 zirconium 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 this chemical.

• **Skin Exposure**

If zirconium compounds get on the skin, wash with soap or mild detergent and water.

• **Breathing**

If a person breathes in large amounts of zirconium 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 zirconium 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 zirconium 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. Liquid containing zirconium oxide, zirconium oxychloride, zirconium tetrachloride, zirconium hydride, or zirconyl acetate should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Zirconium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ZIRCONIUM COMPOUNDS (AS ZIRCONIUM)

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
25 mg/m³ or less	Any dust and mist respirator, except single-use.
50 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any 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.
500 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 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

* U.S. GOVERNMENT PRINTING OFFICE: 1981/661-362