OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CYANOGEN CHLORIDE

INTRODUCTION

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 Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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

SUBSTANCE IDENTIFICATION

- **Formula**

  ClCN

- **Structure**

  N≡CCl

- **Synonyms**

  Chlorcyan; chlorine cyanide; chlorocyanide; chlorocyanogen

- **Identifiers**

  1. CAS No.: 506-77-4
  2. RTECS No.: GT2275000
  3. DOT UN: 1589 15 (for cyanogen chloride containing less than 0.9% water)
  4. DOT label: Poison gas; Flammable gas

- **Appearance and odor**

  Cyanogen chloride is a colorless gas with a pungent, penetrating odor. It is shipped in steel cylinders under its own vapor pressure as a liquefied gas. The odor threshold of cyanogen chloride is 1 part per million (ppm) parts of air.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 61.5
  2. Boiling point (760 mm Hg): 13.8°C (56.8°F)
  3. Specific gravity (water = 1): 1.2 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of cyanogen chloride): 2.16
  5. Melting point: -6°C (21.2°F)
  6. Vapor pressure at 20°C (68°F): 1,000 to 1,010 mm Hg
  7. Solubility: Soluble in water, alcohol, ether, and all organic solvents

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

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

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Moisture, sparks, heat, or flame

2. Incompatibilities: Contact of cyanogen chloride with water, steam, acids, acid salts, or strong oxidizing agents may cause fires or explosions.

3. Hazardous decomposition products: Toxic substances (such as the oxides of nitrogen cyanide, cyanide, chloride ions, and hydrogen cyanide) may be released in a fire involving cyanogen chloride.

4. Special precautions: Crude cyanogen chloride trimerizes violently to cyanuric chloride if catalyzed by traces of hydrogen chloride or ammonium chloride.

Flammability

The National Fire Protection Association has not assigned a flammability rating to cyanogen chloride. However, the Hazardous Materials Identification System (HMIS) developed by the National Paint and Coatings Association assigns cyanogen chloride a flammability rating of 4 (severe fire hazard).

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, carbon dioxide, water spray, fog, or standard foam to fight fires involving cyanogen chloride.

Fires involving cyanogen chloride should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of cyanogen chloride may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Take care not to permit water to contact the cyanogen chloride inside the containers. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving cyanogen chloride. Chemical protective clothing that is specifically recommended for cyanogen chloride may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing may provide limited protection against fires involving cyanogen chloride.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for cyanogen chloride [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.3 ppm (0.6 mg/m^3) as a ceiling limit [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned cyanogen chloride a ceiling limit value of 0.3 ppm (0.75 mg/m^3) [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of severe eye and pulmonary irritation [NIOSH 1992]. The ACGIH limit is based on the risk of irritant, metabolic, and respiratory effects associated with exposure to cyanogen chloride [ACGIH 1993].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to cyanogen chloride can occur through inhalation, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* Cyanogen chloride causes eye, mucous membrane, skin, and upper respiratory tract

irritation in animals. Although experimental data on skin absorption are lacking, this substance is reported to cause systemic toxicity when absorbed through the skin in toxic amounts [NLM 1992]. The LC_{50} in rats is 5,400 mg/m^3 (2,700 ppm) for 3 min; in monkeys, it is 4,400 mg/m^3 (2,200 ppm) for 1 min; and in rabbits, it is 6,000 mg/m3 (3,000 ppm) for 7 min [NIOSH 1993]. Animals acutely poisoned with cyanogen chloride show signs of cyanide poisoning and pulmonary edema (dyspnea, bloody nasal exudate, cyanosis) before death [ACGIH 1991].

2. *Effects on Humans:* Cyanogen chloride is a severe eye, skin, mucous membrane, and upper respiratory tract irritant in humans. Exposure to cyanogen chloride also causes cellular hypoxia, as is the case with other cyanides. Exposure to concentrations of cyanogen chloride below 1 ppm (approximately 0.7 ppm) causes burning of the eyes, lacrimation, and severe blepharospasm, local skin irritation, and marked respiratory tract irritation, with hemorrhagic changes and pulmonary edema [Grant 1986; NLM 1992; ACGIH 1991]. Cyanide also interferes with the cell's ability to utilize oxygen, which leads to cellular hypoxia, headache, dizziness, and signs and symptoms that include seizures and coma. Exposure to a cyanogen chloride concentration of 48 ppm for 30 min or to a 159-ppm concentration for 10 min has caused death in humans [Clayton and Clayton 1982]. Repeated inhalation of low (not further specified) concentrations of cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, and weight loss [NLM 1992]. Workers chronically exposed to cyanide salts during metal heat-treating operations developed enlarged thyroid glands [ACGIH 1991; NLM 1992].

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute exposure to cyanogen chloride may cause burning of the eyes, tearing, and spasms of the eyelids; a bitter, burning taste followed by a feeling of constriction in the mouth; sweating, salivation, nausea, and vomiting; anxiety confusion, vertigo, giddiness, dizziness, and headache; a bright pink or brick-red coloration to the skin; difficult breathing; increased or decreased blood pressure and heart rate; seizures; and an increase in respiratory rate followed by respiratory arrest.

2. *Chronic exposure:* Chronic overexposure to cyanogen chloride may cause dizziness, lung congestion, loss of appetite, mental deterioration, weight loss, and enlargement of the thyroid.

- **Emergency procedures**

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

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

1. *Eye exposure:* Irritation may result. ***Immediately and thoroughly*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Skin irritation or absorption of toxic amounts may result. ***Immediately*** remove contaminated clothing and ***thoroughly*** wash contaminated skin with soap and water for at least 15 min.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.***

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

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

EXPOSURE SOURCES AND CONTROL METHODS

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

—Use in organic synthesis

—Military use as a poison and tear gas

—Use as a warning agent in fumigant gases

—Use in ore refining, in the production of synthetic rubber, and as a metal cleaner

—Use in the Lonza process to produce extremely pure malononitrile

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

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

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

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

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

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

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

MEDICAL MONITORING

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

- **Preplacement medical evaluation**

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

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

- **Periodic medical examinations and biological monitoring**

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

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Thiocyanate, a metabolite of cyanide, can be measured in the plasma and urine of exposed individuals. However, the levels of thiocyanate in these body fluids that correspond to airborne concentrations of cyanogen chloride have not been determined. Therefore, no biological monitoring test acceptable for routine use has yet been developed for cyanogen chloride.

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

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

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne cyanogen chloride is determined by using a coated XAD-2 tube (150/75-mg sections, 20/60 mesh). The coating is 10% (w/w) 2-(hydroxymethyl)piperidine. Samples are collected at a maximum flow rate of 0.2 liter/min. The sample is then treated with toluene to extract the cyanogen chloride. Analysis is conducted by gas chromatography using a nitrogen phosphorus detector. This method is described in the OSHA Computerized Information System [OSHA 1992].

PERSONAL HYGIENE

Cyanogen chloride can be absorbed through the skin in toxic amounts. Therefore, if cyanogen chloride contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with cyanogen chloride should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of cyanogen chloride, particularly its potential to be absorbed through the skin in toxic amounts.

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

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

STORAGE

Cyanogen chloride gas or liquid should be stored in a cool, dry, well-ventilated area in pressurized, airtight containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Cyanogen chloride should not be exposed to direct sunlight. Containers of cyanogen chloride should be protected from shock or physical damage and should be stored separately from water, acids, acid vapors, strong oxidizing agents, heat, sparks, and open flame. Because containers that formerly contained cyanogen chloride may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

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

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Evacuate all nonessential personnel.
4. Ventilate potentially explosive atmospheres.
5. Use water spray to reduce vapors; do not put water directly on the leak or spill area.
6. Do not get water inside container.
7. For small liquid spills, flush area with flooding amounts of water.
8. For large liquid spills, build dikes far ahead of the spill to contain the cyanogen chloride for later reclamation or disposal.

SPECIAL REQUIREMENTS

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

- **Emergency planning requirements**

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

- **Reportable quantity requirements for hazardous releases**

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

The reportable quantity for cyanogen chloride is 10 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

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

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

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

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

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

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Cyanogen chloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 USC 6901 et seq.], and has been assigned EPA Hazardous Waste No. P033. This substance has been banned from land disposal and may be treated by chemical oxidation, wet air oxidation, or incineration. Cyanogen chloride also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

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

RESPIRATORY PROTECTION

- **Conditions for respirator use**

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

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the

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

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing (gloves, boots, aprons, and full-body clothing) should be worn as necessary to prevent any skin contact with cyanogen chloride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to cyanogen chloride permeation; however, butyl rubber is reported to provide no more than 1 hr of resistance against permeation by cyanogen bromide, a chemically similar substance. Since specific test data are not available for cyanogen chloride, the information provided here should be considered as a guideline only. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to cyanogen chloride.

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

Safety glasses, goggles, or face shields should be worn during operations in which cyanogen chloride gas or liquid might contact the eyes. Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with cyanogen chloride. Contact lenses should not be worn if the potential exists for cyanogen chloride exposure.

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