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: COCl2
- 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/m³). 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

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation 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

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 MCA 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

2 Phosgene September 1978

technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety 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

Liberation during openflame cutting of certain metals in presence of chlorinated hydrocarbons

Liberation from synthesis of isocyanates in manufacture of polyurethane plastics; alkyl isocyanates in pesticide manufacture; polycarbonated resins for molded plastics, dyestuffs, and pharmaceuticals

Liberation during fireextinguishing with agents containing chlorinated hydrocarbons

Liberation during sand bleaching operations in glass manufacture

Controls

Insolation of operations from chlorinated hydrocarbons; local exhaust ventilation; personal protective equipment

Process enclosure; local exhaust ventilation

Material substitution; personal protective equipment

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

September 1978 Phosgen∈ 3

rescue 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.

REFERENCES

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

- American Industrial Hygiene Association: "Phosgene," Hygienic Guide Series, Detroit, Michigan, 1968.
- Cucinell, S. A.: "Review of the Toxicity of Long-Term Phosgene Exposure," *Archives of Environmental Health*, 28:272-275, 1974.
- Gross, P., et al.: "Chronic Pneumonitis Caused by Phosgene," Archives of Environmental Health, 10:768-775, 1965.
- International Labour Office: Encyclopedia of Occupational Health and Safety, McGraw-Hill, New York, 1971.
- Jacobs, M.: The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents, Interscience, New York, 1956.
- Manufacturing Chemists Association, Inc.: Chemical Safety Data Sheet SD-95, Phosgene, Washington, D.C., 1
- May, J.: "Solvent Odor Thresholds for the Evaluation of Solvent Odors in the Atmosphere," *Staub-Reinhalt*, 26:9, 385-389, 1966.
- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: Criteria for a Recommended Standard.... Occupational Exposure to Phosgene, HEW Publication No. (NIOSH) 76-137, GPO No. 017-033-00134-1, U.S. Government Printing Office, Washington, D.C., 1976.
- 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.
- Stecher, P. G. (ed.): The Merck Index (8th ed.), Merck & Co., Inc., Rahway, New Jersey, 1968.
- Thienes, C. H., and Haley, T. J.: Clinical Toxicology (5th ed.), Lea and Febiger, Philadelphia, 1972.

4 Phosgene September 1978

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.