

VI. WORK PRACTICES

Strict adherence to stringent and detailed work practices is required if hazardous occupational exposures to phosgene are to be prevented. The properties of phosgene which determine to a large extent the nature of necessary work practices are: (a) the delayed and insidious onset of symptoms due to exposure to low concentrations; (b) an odor threshold which cannot be relied upon to provide an adequate warning; and (c) its irritant effects on tissue, especially the lungs. However, precautions required in the handling and usage of phosgene have much in common with those required for other irritating gases. The work practices specified in this document are derived in large part from phosgene manufacturers' literature [10,133] and the Manufacturing Chemists' Association Chemical Safety Data Sheet SD-95. [1] In addition, work practices prescribed for other irritating gases have been adapted for phosgene wherever pertinent (eg, those published in the Chlorine Manual [134]).

Warning Properties

The American Industrial Hygiene Association [90] stated that the irritant properties of phosgene were insufficient to give warning of hazardous concentrations, and that olfactory fatigue caused personnel working with phosgene to lose their ability to detect low concentrations by smell. Supporting data for these statements were not reported.

The Manufacturing Chemists' Association [1] reported that the odor of phosgene can be recognized by some persons at 0.5 ppm, but that the sense of smell is conditioned by the gas so that the odor can only be detected

briefly at the time of initial exposure. No substantiating data for these statements were cited, but many materials do have the ability to cause odor fatigue.

Leonardos et al [18] investigated the odor thresholds of 53 chemicals. They defined the odor threshold as the first concentration at which all members of a trained panel could recognize the odor of a chemical. Their tests indicated an odor threshold for phosgene of 1.0 ppm. The odor was described as being "hay-like."

In 1938, Wells et al [17] determined threshold odor detection of phosgene in a number of volunteers. Test concentrations were established with a proportioning instrument known as an osmoscope. Three tests run on 56 subjects showed that all subjects detected the odor of phosgene at or below 37.5 mg/cu m (9.4 ppm), 51.8% detected the odor of phosgene at or below 6.1 mg/cu m (1.5 ppm), and that none detected the odor below 1.8 mg/cu m (0.45 ppm).

Macy, [135] summarizing the properties and the physiological action of phosgene, stated that the threshold of odor for phosgene was 4.4 mg/cu m (1.1 ppm). Substantiating data were not included in this report.

It is concluded that the odor of phosgene, when detected, indicates the need for immediate corrective action. However, an absence of odor cannot be relied upon to indicate that exposure does not exist.

Emergencies

Personnel who have escaped from an exposure to phosgene and have inhaled dangerous quantities should be kept warm but not overheated. If possible, they should not be allowed to walk from the scene of overexposure

but should be carried. Exercise may intensify the effects of phosgene, but this has not been definitely established. In any case, physical activity should be limited to keep oxygen requirements at a minimum. Every effort must be made to treat the individual after overexposure occurs and to observe him for the onset of delayed symptoms. All facilities handling phosgene should have compressed, breathing-grade oxygen available. [1,2,10,11]

Phosgene presents no fire or explosion hazard, but high temperatures may rupture containers because of increased hydrostatic pressure. [2] In case of fire, phosgene containers should be removed to a safe place or cooled with water if phosgene is not escaping. [1]

Spills are best controlled with solutions of caustic soda or with ammonia. It has been reported [1] that some manufacturers store one ton of ammonia for each ton of stored phosgene for the purpose of neutralizing liquid spills.

Control of Airborne Phosgene

Phosgene should be used only in completely closed systems. In addition, local exhaust and general ventilation can be effective for control at points of potential escape. [1,2,10,38,58,59,90] Discharges of ventilation systems or of leaking containers may be passed through scrubbers utilizing caustic soda, ammonia, or steam to prevent phosgene from reaching the outdoor atmosphere. [1,2,90,133]

The possibility of phosgene formation must be considered when installing and operating vapor degreasers containing chlorinated hydrocarbons, since under poor operating conditions, these are potential

sources of phosgene. [5,74,136] They should be controlled to prevent exposure of operators to both solvent vapors and phosgene.

During maintenance operations on equipment in which phosgene has been present, there is a potential hazard of exposure to phosgene which is entrapped in the equipment or adsorbed on surfaces or in materials. Respiratory protection should be supplied to maintenance personnel working on equipment that has carried phosgene, unless it can be established that no phosgene is present.

Respiratory Protection

Neither chemical cartridge respirators nor half-face masks are recommended for protection against phosgene. [137] Canister-type gas masks are recommended only for rapid escape from a contaminated area because of the following limitations:

(1) Their useful life is unpredictable because of a number of variables such as breathing rate, ambient humidity, and contaminant concentration. [137]

(2) They cannot be used in atmospheres deficient in oxygen or containing phosgene in concentrations over 2.0% by volume. [137] Therefore, they are not suitable for controlling emergency exposures where the concentration of phosgene and the oxygen content of the air are unknown. [1]

(3) Users of gas masks have depended on the detection of an odor of the atmospheric contaminant to warn them of loss of protection by the canister or to indicate leaks. [1,137] However, phosgene has poor warning properties in low concentrations [1,90] and therefore the odor cannot be

depended upon to indicate a faulty gas mask in time to prevent harm to the wearer.

Training in the use of respiratory protection is required by 29 CFR 1910.134 and is stressed as an essential work practice in occupations involving potential exposure to phosgene. [1,138] Accordingly, a requirement for training is included in the standard. Recognition of the odor of phosgene should be a part of this training. [138]

Gas-mask canisters should be replaced immediately after each use, when the seal is broken, when any leakage is detected, when high breathing resistance develops, or when the recommended shelf life expires, whichever occurs first. [137]

Because of the irritant properties of phosgene, emergency respiratory protection must provide both eye and respiratory protection for the worker. Full-face masks are the only acceptable devices for employees exposed to phosgene leaks or for the protection of personnel who may be exposed to sudden high concentrations of phosgene. Masks connected to air lines or having a self-contained air or oxygen supply can also be used. Pocket- or mouthpiece-type respirators used for escape in some operations [137] are not recommended for that purpose.

Eye Protection

Liquid phosgene is probably a severe eye irritant, [11,139] as discussed in Chapter V. Protection should be provided against accidental splashes of the liquid. [90,108] Vapor concentrations of phosgene which are said to affect the eyes (1-10 ppm) are likely to affect the respiratory system as well. Accordingly, eye and respiratory protection should be combined by use of full-face respiratory protection.

Skin Protection

Liquid phosgene is said to cause severe skin burns, [1,90,139] and although this point is inadequately documented, it is a likely effect as discussed in Chapter V. Skin exposure to liquid phosgene should be prevented by the use of impervious clothing and gloves. Clothing impregnated with phosgene should be removed immediately.

Leak Detection

Continuous monitoring of areas where phosgene exposure can occur is considered essential and should be required when suitable models are available. Such monitors should be attached to alarm systems which will indicate dangerous levels of phosgene. For monitoring purposes phosgene-indicating crayons have been used. [1,10,140] Phosgene detector tubes have been described, [1,2,90] as have test papers, [2,10,90] and commercially available automatic monitor-alarms. [90, RJ Zellner, written communication, November 1974] Holding a bottle of strong ammonia water near a phosgene leak will produce a visible white cloud. [1,2,10,133] However, this should not be done unless the worker is wearing a respirator.

Leak Control

When detected, leaks should be repaired immediately by personnel wearing the proper protective clothing and respiratory protection. Leak repair kits may be assembled [1] or are commercially available. [133] Routine inspection should be scheduled to check pumps, lines, and containers for leaks; this practice is especially important during maintenance operations.[36] Leaking containers should be positioned so that

gas rather than liquid phosgene is discharged from the leak. [133] This results in less discharge of phosgene and the escaping gas cools the remaining phosgene, thus reducing pressure and leakage. Introducing moisture into phosgene can cause increased pressures sufficient to rupture containers [10,11] or can cause leaks through corrosion. [10,11]

VII. RESEARCH NEEDS

Long-term epidemiologic studies of worker populations exposed at or below the recommended environmental limits are needed. Such studies should consider not only the pulmonary effects but also the possible carcinogenic effect of phosgene. As a minimum, these studies should include environmental air measurements, medical histories, pulmonary function studies, histories of known or suspected acute exposures to phosgene, and comparisons with morbidity and mortality information for the general population.

Animal studies should be conducted to document pulmonary or other changes resulting from exposure at low levels of phosgene for extended periods. These studies should also address the issues of carcinogenicity, mutagenicity, and teratogenicity.

A sampling and analytical method for personal monitoring capable of detecting 0.05 ppm or less of phosgene should be developed. The accuracy, sensitivity, and applicability of the method to field situations should be demonstrated by a program of field and laboratory testing.

Existing methods for automatic, continuous monitoring should be tested for sensitivity, accuracy, and specificity by comparison with a reliable standard method. Since one of the primary functions of automatic, continuous monitoring is as a warning device, alarm systems should be developed and tested for reliability.

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