

4.0 Industrial Hygiene and Personal Protective Equipment

Introduction

The information presented in this section is a general composite of best practices and current information about industrial hygiene preventive health measures, standards for exposures and air monitoring; and personal protective equipment selection, training, use and maintenance. The information provided in this section should not be considered as a directive or as an industry standard that readers must adopt or follow. Instead, the information is intended to provide helpful ideas and guidance that users may wish to consider in a general sense (See Section 1.1 *Preface and Legal Notice*). Also included is a reference list of useful resources.

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4.1 Industrial Hygiene

4.1.1 Preventive Health Measures

CAUTION! Odor should not be relied upon to give adequate indication for the presence of phosgene.

Based on a review of existing information, odor references cited in the literature were all rejected or the source was unable to be located (ACGIH, 1989). Aside from this, since the reported odor ranges are generally above the Permissible Exposure Limit (PEL), odor does not provide adequate warning of presence. Additionally, personnel working with phosgene can lose their ability to detect low concentrations by conditioning or deadening of the sense of smell. Exposure assessment programs based on colorimetric indicators (badges) have been developed to identify employees with exposure.

Workers with potential for exposure to phosgene can benefit from receiving instruction periodically in the hazards of the chemical and in safe handling procedures. The development and utilization of control measures helps reduce potential risk for exposure.

4.1.2 Standards for Exposure

The 2017 threshold limit value (TLV®) established by the American Conference of Governmental Industrial Hygienists (ACGIH) for phosgene is 0.1 ppm (volume/volume). The TLV® refers to the airborne concentration and represents the condition under which it is currently believed by the TLV® Committee that nearly all workers may be repeatedly exposed day after day without adverse health effects. It is a time-weighted average (TWA) concentration for an 8-hour workday and 40-hour workweek. It only serves as a guide in the control of health

hazards, and not as a fine line to distinguish between safe and dangerous concentrations. Engineering control measures can be used to maintain very low phosgene exposure concentrations, so that routine exposure too near 0.1 ppm does not occur. Control measures serve a critical function towards eliminating phosgene concentrations in the work place.

The Occupational Safety and Health Administration (OSHA) sets a limit of 0.1 ppm, expressed as an 8-hour time-weighted average. As of 2017, the TLV® and Permissible Exposure Limit (PEL) are the same value.

Based on the 2017 ACGIH TLVs® for Chemical Substances and Physical Agents, limited excursions above the TLV® are permitted for short periods of time. While there is no guidance for a short term exposure level (STEL) or Ceiling (C), ACGIH provides that excursions in worker exposure levels may exceed 3 times the TLV®-TWA for no more than a total of 30 minutes during a workday, but under no circumstances should they exceed 5 times the TLV®-TWA.

The National Institute of Occupational Safety and Health (NIOSH) gives an additional recommendation for short-term excursions. The NIOSH Recommended Exposure Limit (REL) for phosgene excursions above the REL is 0.2 ppm for 15 minutes (NIOSH, 2010). TLVs®, RELs and PELs are subject to change by their associated peer review groups. As with other references in the Guidelines, users must check the current reference for up-to-date information.

It is important to note that the concept of an established time weighted average exposure limit for phosgene may imply that a background level of phosgene in the work place may be considered acceptable practice. This is not true. Member companies use a variety of engineering and work practice controls to minimize risk for even small exposures. Due to the acute toxicity of phosgene, it is not considered safe to operate in conditions where background concentrations of phosgene are present in work place air.

4.1.3 Air Monitoring

Early methods for the detection of phosgene utilized absorption into a solution which changes color (25% 4(4'-nitrobenzyl pyridine) and stabilizes the color (0.5% N-phenylbenzene) (NIOSH, 1977). The absorbance was then read on a spectrophotometer. Sampling efficiency was excellent, but the use of an

impinger had drawbacks. Another method developed by OSHA to provide a simpler, convenient and precise means to monitor occupational exposure to phosgene, utilized sampling tubes containing XAD-2 adsorbent coated with 2-(hydroxymethyl) piperidine. The samples are desorbed with toluene and then analyzed by gas chromatography using a nitrogen selective detector (OSHA, Method No. 61). The early colorimetric methods gave rise to development of diffusion badges.

Badges that change color upon exposure to phosgene are commercially available. They are commonly referred to as dosimetry badges. While dose typically refers to body uptake of contaminant, if the dosimetry badge is worn in the breathing zone, the wearer's exposure is considered their dose. Color change is from white to pink (red) or white to blue. Extremely high concentrations (percent not ppm levels) may cause the color to change back to white again. Badge readings may vary depending on the manufacturer of the badge, the reader of the badge, and other conditions and factors. Badge manufacturers may provide additional details for inclusion in employee training.

Dose is the product of concentration of phosgene in air and time (ppm-minutes) of exposure, $D = C \times T$. Dose is estimated by matching the intensity of color on a badge reader or color wheel (graduated color intensities which correspond to dose (ppm-minutes)). The potential for individuals' color blindness to reds may need to be considered when developing a badge program.

Users can develop written programs including a log of exposures. Absence of exposure is also useful to know in the performance of certain operations and maintenance tasks. Documentation of dose can include details of the event leading to the exposure as well as details of any respiratory protection used. Typical information to record includes the name of the individual who wore the badge, the person entering the information, and the specific circumstances of the event. During training on the use of the badges, inform users that **ALL** exposures be reported immediately. In most cases, exposures warrant an incident investigation and accompanying documentation of that investigation.

Badge placement is an important consideration in a badge program. More useful and reliable results are achieved if the badge is placed in the breathing zone of the individual. When this is done, the subject's breathing zone exposure can be assumed to be their dose unless the individual is wearing respiratory protection. Badges that are affected by ultraviolet (UV) light and water may be adhered under the front brim of the hard-hat. Refer to badge manufacturer's

instructions for specific information. Alternatively, clips can attach the badge to the collar to better secure the badge and still provide representative breathing zone concentration. Wearing badges under additional personal protective equipment (PPE) (chemical suits, bunker gear, etc.) and badges worn on the back of the hard-hat can hinder the effectiveness of the badge.

Users may also consider including Standard Operating Procedure or Job Safety Information, instructions on the proper use of badges and medical reporting procedures in the written program. Follow the badge manufacturer's recommendations for use. It must be emphasized again, however, report ANY phosgene exposure for investigation keeping in mind the toxicity and the hazard potential of phosgene.

In some circumstances, it may be necessary to employ instrumentation in the event phosgene is released in areas where it could enter a building (e.g., intake through the heating, ventilating and air-conditioning (HVAC) system, conduit penetrations, etc.). Detection of trapped phosgene vapors after a release is important because vapors could pose a threat to building occupants in the vicinity or persons downwind of a release.

Remote optical sensing systems such as Fourier Transform Infrared (FTIR) may be useful to monitor for phosgene down a long path, rather than detecting its presence at a single point.

4.2 Personal Protective Equipment (PPE)

4.2.1 General

The primary target organ for phosgene exposure is the lung; for liquid phosgene it can be the eye, skin, and lung. Consider establishing engineering and work practice controls to help guard against potential exposure because the odor of phosgene may not give adequate warning as to the potential exposure hazard due to the relatively high odor threshold and the odor not being unpleasant or irritating. Phosgene fatalities have occurred from overexposure, sometimes with few, if any, initial symptoms.

Handling phosgene in completely closed processing systems helps minimize exposure. In the event of a release of phosgene, the immediate evacuation of the area, and entering the area only with the use of appropriate respiratory

protective equipment will minimize potential exposures. (See Section 4.2.8 for additional information on respiratory equipment). It is beneficial to have several sets of respiratory protective equipment available at all times stored outside of, but near to, the area where phosgene is used.

Workers can benefit from instructions on how to avoid or minimize breathing phosgene in areas where they may be exposed to the gas. Items that help the worker avoid breathing the gas include a pressure demand full-face supplied air respirator in combination with an auxiliary self-contained breathing apparatus or SCBA when it is expected that phosgene may escape. Familiarize workers with the location, operation, limitations, and the duration of use of respiratory protective equipment (29 CFR 1910.134(c)(1)(vii & viii)). Training and handling protocols for phosgene will have incident reporting requirements for any suspected phosgene exposure (29 CFR 1910.199 (m)). Liquid exposures will also consider the cryogenic properties of a liquid phosgene exposure to skin or eyes as well as the need to decontaminate protective equipment or clothing before downgrading respiratory protective measures. Phosgene gas/vapors may remain a hazard after signs of liquid phosgene have been removed or evaporated. Phosgene detection devices are essential tools in determining effective decontamination of equipment and clothing, (See Section 4.2.12 - Decontamination).

Personal protective equipment (PPE) complements, but does not substitute for safe working conditions, adequate process control, ventilation and proper conduct by employees working with phosgene. However, in some instances, PPE is the only practical means of protecting the worker in emergency situations and while performing tasks where engineering controls are not sufficient.

An appropriate choice in selection and use of personal protective equipment will normally be dictated by the total situation, rather than by the toxic properties of phosgene alone. These situations may also involve other hazardous materials or normally innocuous materials that can magnify potential concerns associated with phosgene. Therefore, the following information on PPE is to be considered as a reference point for general guidance. Users need to select appropriate personal protective equipment based on their specific needs and circumstances. Other chemicals or factors may require the use of additional protection. Except in an extreme emergency situation, no one should be given personal protective equipment without suitable training in its use.

CAUTION: It is important to consider all the chemicals potentially present with phosgene when selecting PPE.

4.2.2 Availability and Use

Where it is located, how it is cared for, and how it is chosen are important considerations for use of PPE. Companies engaged in frequent use of PPE may assign personnel, provide facilities, and establish programs for suitable care, disposal, decontamination and repair of PPE (29 CFR 1910.132(f)(1)).

4.2.3 Training

Companies provide training for employees using PPE in phosgene service. It is important for employees to be appropriately experienced in the use of the relevant PPE prior to its use in phosgene service. PPE manufacturers can often provide information to develop such training materials and programs (29 CFR 1910.132(f)(1)).

4.2.4 Protective Clothing

Where the presence of liquid phosgene is anticipated protection against the cryogenic liquid may be needed.

Chemical resistant suits are often used for protection against liquid splash. In addition, as one possible reference source, users may consider information provided from the Quick Selection Guide to Chemical Protective Clothing (Forsberg et al., 2014).

The Quick Selection Guide provides specific recommendations for exposures >4 hours and for exposures >8 hours.

The Quick Selection Guide to Chemical Protective Clothing also provides that the following PPE designations would be appropriate where contact with Phosgene is anticipated:

- Level A - highest level of respiratory, skin (fully encapsulating suit) and eye protection, or
- Level B - highest level of respiratory protection, less skin protection than Level A (one or two piece chemical resistant clothing) may be chosen depending upon need and availability.

4.2.5 Foot Protection

Leather or rubber safety shoes with built-in steel toe caps provide extra protection against injury for workers handling cylinders of phosgene. Rubber shoes may be worn over leather safety shoes where liquid phosgene may be encountered. It will be necessary to thoroughly clean or, in some cases, to discard footwear that has become contaminated with phosgene.

4.2.6 Hand Protection

Hand protection should be considered to protect against cryogenic burns if the possibility of contact with liquid phosgene exists.

4.2.7 Eye Protection

Phosgene exposure is corrosive to the eyes. Safety glasses with side shields help protect personnel during routine operations. When there is splash potential or concentrations that may cause eye irritation, a full-face supplied air respirator will provide a greater degree of eye protection than goggles.

4.2.8 Respiratory Protection

Personnel are required to be medically approved to wear respiratory protection (29 CFR 1910.134(c)(1)(ii)). Respiratory protection for medically approved personnel is needed because serious, even fatal exposure to phosgene may occur in tanks during equipment cleaning and repairs, when decontaminating areas following spills, or when failure of piping or equipment occurs. To help prevent injury, respiratory protection and training in its use can be provided to employees who may be subject to such exposures. Examples of available types are described below.

The Occupational Safety and Health Administration (OSHA) has provided requirements for respiratory protective equipment. (See Title 29 CFR 1910.134 as amended). Such equipment is carefully maintained, inspected, cleaned and disinfected at regular intervals and before use by another person. Consult a reputable safety equipment representative for details on the proper use of approved equipment.

In its Pocket Guide to Chemical Hazards, the National Institute for Occupational Safety and Health (NIOSH) recommends supplied air up to a concentration of 1 ppm phosgene (NIOSH, 2010). NIOSH also provides that in concentrations up

to 2 ppm, (maximum use concentration), it is recommended that persons use a full face supplied air respirator or full face self-contained breathing apparatus (SCBA). For emergencies or planned entry into unknown concentrations or Immediately Dangerous to Life or Health (IDLH) conditions, NIOSH recommends a pressure demand full-face supplied air respirator in combination with an auxiliary self-contained breathing apparatus or SCBA. The IDLH concentration is 2 ppm.

Note: The use of a pressure demand full-face supplied air respirator (SCBA) can help reduce the risk for exposure if the face seal of the respirator were compromised.

Note: In addition to a dosimetry badge worn in the breathing zone, use of a dosimetry badge or phosgene detection paper worn inside a full-face respirator may be used to indicate presence of phosgene inside the respirator mask.

Respiratory Protection Options for Entry and Emergency

Escape

The following list includes examples of available respiratory protection devices which users may consider as they select a level of protection for entry. All regulators on the equipment below are of the pressure demand type.

- Supplied air breathing apparatus with auxiliary self-contained breathing apparatus.
- Self-contained breathing apparatus.
- Self-contained breathing apparatus with communication system.
- Supplied air breathing apparatus with in-line egress unit with communication system.
- Supplied air breathing apparatus (overpressure) 2/3 L bottle.

The following includes examples of, but is not limited to, available respiratory protection devices for emergency escape which users may consider as they select a level of protection.

- Supplied air egress hoods/respirators.
- Hooded respirator with organic vapor/acid gas cartridge.
- Other configurations of eye and respiratory protection based on a current assessment for the potential of exposure influenced by location, worst

anticipated concentration, and/or other process considerations to ensure safe egress is possible.

NIOSH and Mine Safety and Health Administration (MSHA) have approved the use of air purifying, full face respirators for escape purposes only. Each company performs their own hazard analysis for emergency egress.

4.2.8.1 Supplied Air Considerations

Handling phosgene often necessitates use of supplied air breathing systems. Where it is prudent to use a separate supply of breathing air rather than relying on ambient air, the following items may be of assistance with regard to the quality of supplied air.

Breathing air quality is discussed in 29 CFR 1910.134(i). Refer to regulatory text for the potential updates and further detail. The specification originated with the Compressed Gas Association (CGA) Commodity Specification G-7.1 (1997).

Breathing air is produced by: (1) compressing ambient air, or (2) synthesizing (blending) gases. Regardless of the method used, verifying the air quality before use helps prevent potential problems. For more information, refer to CGA (Compressed Gas Association) specification for Grade D air purity.

During validation, evaluate whether the oxygen content is maintained between 19.5-23.5%. (See 29 CFR 1910.134 regarding oxygen content). Any deviation from an actual concentration of 20.9 % can signal cause for follow-up activity.

Compressed air breathing systems must be adequately designed, alarmed, and maintained for the purpose. Key issues to consider are alarm systems, materials of construction, commissioning, maintenance, back-up systems, and the location of intake to avoid potential for contaminants.

4.2.9 Head Protection

The use of hard hats helps protect against head injuries that may result from falling objects or from running into low piping or other equipment.

4.2.10 Storage of PPE for Phosgene Service

Making emergency escape respirators readily available or carried by personnel in areas where escape from phosgene may be required reduces potential risks. It is desirable that emergency response equipment (respirators, chemical protective clothing, etc.) be located in strategic locations to help facilitate prompt response, yet also be sufficiently removed from the phosgene process area so as not to be involved in an emergency should one arise.

4.2.11 Maintenance of PPE for Phosgene Service

Refer to the manufacturer's instructions / recommendations for PPE use, inspection and maintenance. Checklists for inspections are often available from the manufacturer. Federal law may mandate inspection frequencies (e.g., OSHA 29 CFR 1910.134(h)(3)).

4.2.12 Decontamination

If phosgene contamination on clothing is present, emergency response personnel should take precautions including the wearing of appropriate respiratory protection while removing any contaminated clothing. Such clothing can be placed immediately in an airtight container until it can be decontaminated. Exposed persons may require the provision of respiratory protection until outside the contaminated area and their contaminated clothing is removed.

It may be necessary that phosgene contaminated clothing and equipment are sealed in an airtight container and disposed of as hazardous waste if the contamination is the result of an emergency response action or a spill and cannot be decontaminated.

CAUTION! The decontamination options listed below are only intended for PPE and other equipment. Care is needed to avoid contacting human skin with these solutions.

Decontamination of PPE and other equipment has been accomplished through such means as:

- Immersion in ammonia water solution.
- Immersion in a soda ash in water solution.

- Washing in soap and water.

Verifying decontamination by available means (e.g., use of phosgene detection devices) **BEFORE** respiratory protection is removed can help reduce risks of exposure.

4.2.13 Line Breaking and/or Vessel Entry

Both line breaking and confined space entry may introduce additional risk to employees. The following practices have been used previously although more stringent practices may be required:

- Restrict entry of unauthorized personnel (barricade area).
- Level A or Level B PPE during initial line-breaking.
- Check equipment to verify “clean” atmosphere before downgrading protection. See Monitoring Instrumentation section.

CAUTION! “Pockets” of phosgene may be trapped in process fluids, solids, or low dips in pipe or equipment. It is important to consider this issue before downgrading PPE.

Note: Consider whether the possibility of liquid phosgene exposure exists, and take appropriate precautions.

4.2.14 PPE Use During an Accidental Release

During a gas leak or liquid spill, the highest level of respiratory protection may be required for entry into the area (see Section 4.2.8 for further information). Consider use of either Level A or Level B skin protection (see Section 4.2.4 for further information).

Note: Phosgene may contaminate equipment and PPE, and can be a hazard if breathed from these secondary sources.

4.2.15 Handling of Phosgene Badges that have Detected an Accidental Exposure

Phosgene badges that have detected an unprotected human exposure should be removed and bagged after the person is clear of potential, continuing exposure. Should the exposed worker need to don respiratory protection and re-enter the contaminated area, the first badge should be secured in an uncontaminated place and a second badge used. The dose measurements provided by these badges will be essential data for medical assessment and treatment decisions and should be preserved. The data on the worker's dose will also be valuable to subsequent incident investigations.

References

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