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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4.1.1 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 detection ranges are generally greater than the OSHA Permissible Exposure Limit (PEL). Therefore, odor does not provide an adequate warning of presence of phosgene. Additionally, personnel working with phosgene can lose their ability to detect low concentrations by conditioning of the sense of smell or olfactory fatigue. 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 Occupational Safety and Health Administration (OSHA) sets a limit of 0.1 ppm, expressed as an 8-hour time-weighted average. 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 are typically used to maintain very low phosgene exposure concentrations, so that routine exposure approaching 0.1 ppm does not occur. Control measures serve a critical function towards eliminating phosgene

concentrations in the workplace.

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). 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 incorrectly imply that a background level of phosgene in the workplace may be considered acceptable practice. 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 workplace 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 the body's 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 facility program development and awareness.

Dose is the product of concentration of phosgene in air and time (ppm-minutes) of exposure, D = C × 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.

Exposure logs are a component of a written phosgene monitoring program. Absence of exposure is also useful information 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 are to be reported immediately. In all cases, phosgene exposure warrants an incident investigation and accompanying documentation of that investigation.

Badge placement is an important consideration in a badge program. Badges worn in the subject's breathing zone can be assumed to best reflect their exposure dosage unless the individual is wearing respiratory protection. Badges that can be potentially affected by ultraviolet (UV) light and water may be attached under the front brim of the hard-hat to aid in protecting the badge from these elements while maintaining the badge's position in the breathing zone. Refer to badge manufacturer's instructions for specific information. Alternatively, clips or pins can attach the badge to the shirt collar 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 will not adequately represent the concentration within an individual's breathing zone.

Documented procedures and user training are typical components of monitoring programs. Follow the badge manufacturer's recommendations for use.

Instrumentation may provide an early warning 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.

4.2 Personal Protective Equipment (PPE)

4.2.1 General

The primary target organ for a phosgene exposure is the lungs. In the liquid state, phosgene can also cryogenically affect tissues in the eyes, and skin. Establishing engineering and work practice controls to help guard against both potential exposure pathways are common. As previously noted, 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 at harmful concentrations. Phosgene fatalities have occurred from overexposure in some instances with few, if any, initial symptoms.

Handling phosgene in completely closed processing systems helps minimize exposure. See section 6 of these Guidelines for further information on closed processing systems and equipment.

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.

Workers can benefit from instructions on how to avoid or minimize breathing phosgene in areas where they may be exposed to the gas. 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 1910.1919 (m)). For liquid exposures, 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).

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.

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 the use of PPE 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 using PPE in phosgene service will have a training program that is compliant with the overriding regulations. 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.

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 exposures. 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 gas and liquid is corrosive to the eyes. Eye protection will typically involve a full-face respirator. Gas tight googles may provide eye protection for escape purposes but are not typically a good barrier for use of any duration in a corrosive environment.

4.2.8 Respiratory Protection

Personnel are required to be medically approved to wear respiratory protection (29 CFR 1910.134(c)(1)(ii)).

To help prevent injury, respiratory protection and training in its use is 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). Such equipment is carefully maintained, inspected, cleaned and disinfected at regular intervals and before use by another person. Development of a respiratory program will typically involve a safety professional familiar with applicable regulations and available equipment. Consult a reputable safety equipment representative that will provide 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, 2019). 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.
- Supplied air breathing apparatus with in-line egress unit.

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.

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.

Breathing air may be 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.

Prior to use, consider verifying the oxygen content. While concentrations between 19.5-23.5% are acceptable (reference 29 CFR 1910.134 regarding oxygen content), any deviation from an actual concentration of 20.9 % can signal the need for a follow-up activity.

Compressed air breathing systems must be adequately designed, alarmed, and maintained for the purpose. Some key items to consider are set-point alarm systems, materials of construction, commissioning, maintenance, back-up systems, and the location of source air 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. Some head protection configurations are designed to be worn with respiratory protection. See your safety equipment supply representative for options to consider.

4.2.10 Storage of PPE for Phosgene Service

Having emergency escape respirators readily available is a good practice for phosgene handling facilities. Readily available may involve well placed inventories of escape respirators, or policies to have escape respirators carried by personnel in areas where escape from phosgene may be required. Facilities can consider requirements for emergency escape respirators to be carried by personnel working in areas where egress can be impeded due to location or work activity, (i.e.; working in elevated position such as a scissors lift or for work performed on a pipe bridge). It may also be beneficial to have emergency response equipment (respirators, chemical protective clothing, etc.) in strategic locations within the facility to facilitate a more prompt response. Considerations to have response equipment also sufficiently removed from the phosgene process area can be beneficial so as not to be involved in an emergency hot zone should the need for response 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 (reference OSHA 29 CFR 1910.132).

4.2.12 Decontamination

Phosgene contamination on clothing and protective equipment can pose a danger to responders as well as the individual bearing the contaminated equipment. Emergency response personnel should take precautions including the wearing of appropriate respiratory protection while removing any contaminated clothing or equipment. Contaminated items can be placed immediately in an airtight container until they can be decontaminated. Exposed persons will likely require the provision of respiratory protection until the decontamination process is complete.

It may be necessary that phosgene contaminated clothing and equipment be disposed of as hazardous waste if the contamination is the result of an emergency response action 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.

Decontamination activities will involve following a procedure for protecting individual responders from exposure to phosgene. Verifying decontamination by available means (e.g., use of phosgene detection devices) **BEFORE** respiratory protection is removed will be an integral step in minimizing the risks of exposure.

4.2.13 Line Breaking and/or Vessel Entry

Both line breaking (opening of equipment that formerly contained or may contain phosgene) and confined space entry situations have the potential to introduce risk to workers. 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 a "clean" atmosphere before downgrading protection. See Monitoring Instrumentation section.

CAUTION! "Pockets" of phosgene may be trapped in process fluids, solids, or low point sections in pipe, inside valves bodies or inside equipment cavities. It is important to consider these hazards as well as the strength of the layers of protection from these situations before downgrading PPE.

4.2.14 PPE Use During an Accidental Release

During a gas or liquid release 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). See Section 5 of the Phosgene Safe Practices Guidelines for Emergency Response considerations. As previously noted, phosgene may contaminate equipment and PPE, and can be a hazard if breathed from these secondary sources during exit from the release area and during decontamination

activities.

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 and closely controlled by the company. The data on the worker's dose will also be valuable to subsequent incident investigations.

References

Forsberg, Krister, and Mansdorf, S.Z., Quick Selection Guide to Chemical Protective Clothing, 6th Edition, June 2020.

National Institute of Occupational Safety and Health, Pocket Guide to Chemical Hazards, 2019.

NIOSH, Manual of Analytical Methods, 2nd Ed., Vol. 2, 1977.

Occupational Safety and Health (OSHA), Personal Protective Equipment. Title 29 CFR 1910.132

Occupational Safety and Health Administration (OSHA), Requirements for Respiratory Protective Equipment. Title 29 CFR 1910.134

OSHA Sampling and Analytical Methods, Method No. 61.