4.0 Industrial Hygiene and 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.

Contents

4.1 Industrial Hygiene

4.1.1 Preventive Health Measures

CAUTION! It is important that odor not be relied upon to give adequate indication of 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 risks.

4.1.2 Standards for Exposure

The 2014 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 2014, the TLV® and Permissible Exposure Limit (PEL) are the same value.

Based on the 2014 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, 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 implies that a background level of phosgene in the work place could be considered an acceptable practice. Due to the toxicity of phosgene, member companies use a variety of engineering and work practice controls to eliminate the risk of over exposures. 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. 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 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 is a factor that can be addressed in the development of a badge program.

Users can develop written programs including a log of exposures or possibly lack of exposures. Documentation of dose can include details of the event leading to the exposure as well as details of any respiratory protection used. Useful information to record includes the name of the individual who wore the badge, the person entering the information, and the 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.

Placement of badges can be an important element in a badge program. More useful and reliable results can be achieved if the badge is placed in the breathing zone of the individual. 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) (slicker suits, bunker gear, etc.) and badges worn on the back of the hard-hat could hinder the badges’ effectiveness.

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

Colorimetric paper can be placed as a mechanism for low level leak detection, especially in open-air environments where tiny leaks may escape detection using hand held monitors, area monitors, or ammonia sprays. Colorimetric paper can be placed and remain for long periods of time (subject to the manufacturer's recommendations for maximum sampling time) to identify low concentrations of phosgene. The lower detection limit of some direct reading instruments may be insufficient to detect very small leaks. Colorimetric paper is also used to confirm adequate clearance and decontamination of equipment prior to opening. Colorimetric badges are reserved for personal dose measurement, and are not designed to confirm adequate clearance and decontamination of equipment because it could introduce opportunity for a misinterpretation of the badge that could result in erroneous exposure conclusions.

Other types of portable and fixed monitoring systems are also available which use either electrochemical cell detectors or a version of the colorimetric chemistry mentioned above. Instrumentation utilizing paper tape chemistries are usually very specific to phosgene. Electrochemical cell detectors may have cross-sensitivity to a number of contaminants typically found in industrial settings (e.g., sulfur compounds and hydrochloric acid (HCl) gas). Filters can help minimize the problem. It is beneficial to discuss this matter with the manufacturers of all these devices, especially where false indication of phosgene could impact your employees, neighboring industries, or the community.

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 path openings, 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

Because the odor of phosgene may not give adequate warning as to the potential exposure hazard due to the high odor threshold and the odor not being unpleasant or irritating, the establishment of engineering controls and work practices help protect against potential risks. 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, reduces potential concerns. (See Section 4.2.8 for additional information on respiratory equipment). It is beneficial to have several sets of 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. Other items may include: equipping and instructing in the use of a pressure demand full-face supplied air respirator in combination with an auxiliary self-contained breathing apparatus or SCBA when it is known that phosgene may escape; familiarizing workers with the location, operation and limitations on the duration of use of respiratory protective equipment; and reporting immediately any episode in which the gas was breathed or of contact of the skin or eyes with liquid phosgene.

Personal protective equipment serves to compliment, but not substitute for safe working conditions, adequate process control, ventilation and proper conduct by employees working with phosgene (engineering controls). However, in some instances, it 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 equipment is to be considered as a potential 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 extreme emergencies, 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

Location, care and selection of appropriate PPE are dictated by the proposed use of the equipment. Companies have assigned personnel, facilities and programs for suitable care, decontamination and repair of all equipment.

4.2.3 Training

Companies provide training so that employees using PPE in phosgene service are appropriately experienced in the use of the relevant PPE prior to its use in phosgene service. Consult the manufacturer recommendations where provided.

4.2.4 Protective Clothing

Where the presence of liquid phosgene is anticipated or in an emergency response situation where either a high concentration of phosgene gas and/or liquid may be present, protection against the cryogenic liquid may be needed. Phosgene gas is not chemically irritating to the skin, but can easily permeate clothing and equipment, which can later expose personnel if appropriate decontamination procedures are not followed.

Chemically resistant suits (“slicker 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., 2007).

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, the use of a full-face supplied air respiratory protection provides greater safeguards.

4.2.8 Respiratory Protection

Users may require that only persons who are medically approved to wear respiratory protection be allowed to work in areas where they may be exposed to phosgene. Serious, even fatal exposure to phosgene may occur in tanks during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. 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 reliable safety equipment dealer 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 supplied air respirator or self-contained breathing apparatus. 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 of exposure should the face seal of the respirator be compromised.

Note: Use of dosimeter badge paper inside of a full-face respirator may be utilized to indicate if phosgene has entered the 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 list 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 bottle.
- Hooded respirator with organic vapor/acid gas cartridge.
- Mouth-bit respirator with acid gas cartridge.

The odor warning properties of phosgene preclude approval by NIOSH and Mine Safety and Health Administration (MSHA). Each company performs their own hazard analysis for emergency egress.

4.2.8.1 Supplied Air Considerations

Handling phosgene often necessitates use of supplied breathing air 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 possibility 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 person 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 20% 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.
- 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: Maintenance workers should 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

American Conference of Governmental Industrial Hygienists, Odor Thresholds for Chemicals with Established Occupational Health Standards, 1989.

American Conference of Governmental Industrial Hygienists, TLVs® and BEIs® Publication, 2014.

Forsberg, Krister, and Mansdorf, S.Z., Quick Selection Guide to Chemical Protective Clothing, 5th Edition, June 2007. Available at http://www.wiley.com/WileyCDA/WileyTitle/productCd-0470146818.html

National Institute of Occupational Safety and Health, Pocket Guide to Chemical Hazards, 2010. Available at http://www.cdc.gov/niosh/npg/npgd0504.html

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

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

OSHA Sampling and Analytical Methods, Method No. 61. Available at http://www.osha.gov/dts/sltc/methods/organic/org061/org061.html.