Occupational Health Guideline for Phosphorus Trichloride

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: PCl₃
• Synonyms: Phosphorus chloride
• Appearance and odor: Colorless to yellow fuming liquid with an odor like hydrochloric acid.

PERMISSIBLE EXPOSURE LIMIT (PEL)
The current OSHA standard for phosphorus trichloride is 0.5 part of phosphorus trichloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3 milligrams of phosphorus trichloride per cubic meter of air (mg/m³). The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for phosphorus trichloride from 0.5 ppm to 0.2 ppm.

HEALTH HAZARD INFORMATION
• Routes of exposure
Phosphorus trichloride 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: Phosphorus trichloride is a severe irritant of the eyes, mucous membranes, and skin and may produce severe burns. Inhalation of the vapor may cause irritation of the respiratory tract. It may produce severe breathing difficulties which may be delayed as much as a day in onset. Phosphorus trichloride on contact with the eyes may produce severe burns with permanent eye damage. Swallowing phosphorus trichloride may produce burns of the mouth, throat, and stomach.
2. Long-term Exposure: Repeated inhalation of phosphorus trichloride may cause chronic cough and wheezing.
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 phosphorus trichloride.
• Recommended medical surveillance
The following medical procedures should be made available to each employee who is exposed to phosphorus trichloride 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, skin, eyes, and kidneys should be stressed.
   —14" x 17" chest roentgenogram: Phosphorus trichloride causes lung damage in humans. Surveillance of the lungs is indicated.
   —FVC and FEV (1 sec): Phosphorus trichloride causes delayed pulmonary edema. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.
2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.
• Summary of toxicology
Phosphorus trichloride vapor is a severe irritant of the eyes, mucous membranes, and skin. These effects result primarily from the action of the strong acids, hydrochloric acid and acids of phosphorus, formed with water. In rats, the LC50 was 104 ppm for 4 hours; at autopsy, the chief finding was nephrosis; pulmonary

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

September 1978
damage was negligible. Inhalation by humans could be expected to cause injury ranging from mild bronchial spasm to severe pulmonary edema; the onset of severe respiratory symptoms may be delayed for 2 to 6 hours, and after moderate exposure the onset may not occur until 12 to 24 hours later. Prolonged or repeated exposure to low concentrations may induce chronic cough and wheezing; pulmonary changes are non-fibrotic and non-progressive. Phosphorus trichloride causes severe burns in contact with the eyes, skin, or mucous membranes. Although ingestion is unlikely to occur in industrial use, it will cause burns of the mouth, throat, esophagus, and stomach.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 137.4
  2. Boiling point (760 mm Hg): 75.9 C (168 F)
  3. Specific gravity (water = 1): 1.57
  4. Vapor density (air = 1 at boiling point of phosphorus trichloride): 4.75
  5. Melting point: –112 C (–169 F)
  6. Vapor pressure at 20 C (68 F): 100 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F):
     Reacts violently to form hydrogen chloride
  8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**
  1. Conditions contributing to instability: Heat may cause containers to burst. Containers may burst if water enters them.
  2. Incompatibilities: Contact with water or alcohol may cause fires and explosions, particularly when in contact with combustible organic matter. Phosphorus trichloride reacts with chemically active metals such as sodium, potassium, and aluminum or with strong nitric acid.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosphine, diphosphine, phosphoric acid, and carbon monoxide) may be released when phosphorus trichloride decomposes.
  4. Special precautions: Phosphorus trichloride will attack some forms of plastics, rubber, and coatings. In the presence of moisture, phosphorus trichloride will severely corrode most metals.

- **Flammability**
  1. Not combustible

- **Warning properties**
  1. Odor Threshold: No quantitative information is available concerning the odor threshold. The MCA notes that this substance has a pungent odor.
  2. Eye Irritation Level: Grant states that “experi-

mentally in cats a concentration of 2 to 4 ppm in air in the course of 6 hours has caused conjunctivitis.”

3. Other Information: Grant points out that the vapors are irritating to the respiratory tract also. The Documentation of TLV’s states that a concentration of 0.7 ppm “was somewhat irritating to animals.”

4. Evaluation of Warning Properties: Since phosphorus trichloride causes irritation at only 0.7 ppm, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**
  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 employer).

- **Method**
  At the time of publication of this guideline, no measurement method for phosphorus trichloride had been published by NIOSH.

- **Method**

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 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, gloves, face shields (eight-inch
can be discarded or until provision is made for the removal of phosphorus trichloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phosphorus trichloride, the person performing the operation should be informed of phosphorus trichloride's hazardous properties.

* Where there is any possibility of exposure of an employee's body to liquid phosphorus trichloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
* Non-impervious clothing which becomes contaminated with phosphorus trichloride should be removed immediately and not reworn until the phosphorus trichloride 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 phosphorus trichloride contacting the eyes.
* Where there is any possibility that employees' eyes may be exposed to liquid phosphorus trichloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

**SANITATION**

* Skin that becomes contaminated with phosphorus trichloride should be immediately washed or showered to remove any phosphorus trichloride.

**COMMON OPERATIONS AND CONTROLS**

The following list includes some common operations in which exposure to phosphorus trichloride may occur and control methods which may be effective in each case:

<table>
<thead>
<tr>
<th>Operation</th>
<th>Controls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use during synthesis of plasticizers and intermediates; and production of intermediates and during chemical synthesis of dyes, pharmaceuticals, other chlorinating agents, and other organic chemicals</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Use in synthesis of pesticide intermediates and surfactants</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
</tr>
<tr>
<td>Use during deposition of metallic coatings; use in treatment of polypropylene before drying in manufacture of knitted fabrics</td>
<td>Process enclosure; local exhaust ventilation; personal protective equipment</td>
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</tbody>
</table>

**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 liquid phosphorus trichloride or strong concentrations of phosphorus trichloride vapors get 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 liquid phosphorus trichloride gets on the skin, immediately flush the contaminated skin with water. If liquid phosphorus trichloride soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

* **Breathing**
  If a person breathes in large amounts of phosphorus trichloride, 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 liquid phosphorus trichloride has been swallowed and the person is conscious, give him large quantities of water immediately to dilute the phosphorus trichloride. Do not attempt to make the exposed person vomit. 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 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, LEAK, AND DISPOSAL PROCEDURES**

* Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
* If liquid phosphorus trichloride is spilled or leaked, the following steps should be taken:
  1. Ventilate area of spill or leak.
  2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material, or;
  3. Cover with sodium bicarbonate or an equal mixture of soda ash and slaked lime, dilute carefully with a small spray of water, then excess water, and dispose in a secured sanitary landfill.

* Waste disposal method:
  Phosphorus trichloride may be disposed of by absorbing in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill or as in 3 above.
RESPIRATORY PROTECTION FOR PHOSPHORUS TRICHLORIDE

<table>
<thead>
<tr>
<th>Condition</th>
<th>Minimum Respiratory Protection* Required Above 0.5 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Concentration</td>
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<tr>
<td>25 ppm or less</td>
<td>Any chemical cartridge respirator with a full facepiece and cartridge(s) containing non-oxidizable sorbents and providing protection against phosphorus trichloride.</td>
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<tr>
<td></td>
<td>A gas mask with a chin-style or a front- or back-mounted canister containing non-oxidizable sorbents and providing protection against phosphorus trichloride.</td>
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<tr>
<td></td>
<td>Any supplied-air respirator with a full facepiece, helmet, or hood.</td>
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<tr>
<td></td>
<td>Any self-contained breathing apparatus with a full facepiece.</td>
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<tr>
<td>50 ppm or less</td>
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<tr>
<td>Greater than 50 ppm or entry and escape from unknown concentrations</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
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<tr>
<td></td>
<td>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.</td>
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<tr>
<td>Fire Fighting</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
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<tr>
<td>Escape</td>
<td>Any gas mask containing non-oxidizable sorbents and providing protection against phosphorus trichloride.</td>
</tr>
<tr>
<td></td>
<td>Any escape self-contained breathing apparatus.</td>
</tr>
</tbody>
</table>

*Only NIOSH-approved or MSHA-approved equipment should be used.