Occupational Health Guideline for p-Phenylene Diamine

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: $C_6H_8N_2$
- Synonyms: p-Diaminobenzene; 1,4-diaminobenzene
- Appearance: White to light purple or brown solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-phenylene diamine is 0.1 milligram of p-phenylene diamine per cubic meter of air (mg/m³) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

p-Phenylene diamine 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: p-Phenylene diamine may cause irritation of the throat.

2. Long-term Exposure: Repeated or prolonged exposure may cause allergy with asthma or skin rash.

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 p-phenylene diamine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to p-phenylene diamine 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. Persons with a history of asthma, allergies, or known sensitization to p-phenylene diamine would be expected to be at increased risk from exposure. Examination of the respiratory system should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

p-Phenylene diamine dust is a skin and respiratory system sensitizer and may produce bronchial asthma and dermatitis in exposed workers. In cats, the minimal fatal peroral dose was 0.1 g/kg. Solutions administered orally or parenterally to animals caused a peculiar and selective edema of the conjunctivae, nose, lips, tongue, and neck. Inflammatory reactions of the pharynx and larynx have been reported in workers. Very small quantities of the dust have caused asthmatic attacks in workers after periods of exposure ranging from 3 months to 10 years. A dilute aqueous solution placed in the eye of a rabbit caused mild transient conjunctival edema. This compound may cause contact dermatitis through sensitization.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 108.1
2. Boiling point (760 mm Hg): 267 C (512 F)
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of p-phenylene diamine): 3.71
5. Melting point: 141 C (286 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): 4.7
8. Evaporation rate (butyl acetate = 1): Data not

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available

- **Reactivity**

1. Conditions contributing to instability: Heat; light
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving p-phenylene diamine.
4. Special precautions: None

- **Flammability**

1. Flash point: 155.5 C (312 F) (closed cup)
2. Autoignition temperature: Data not available
3. Minimum explosive concentration: 0.025 g/l
4. Extinguishant: Carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of p-phenylene diamine.
2. Eye Irritation Level: Gleason reports that p-phenylene diamine in the eye produces "chemosis, lacrimation, exophthalmos ophthalmia, and even permanent blindness." Kirk and Othmer report that p-phenylene diamine "is responsible for keratoconjunctivitis, swollen conjunctiva, and eczema of the eyelids." Grant provides similar information, but no quantitative data are given.
3. Evaluation of Warning Properties: p-Phenylene diamine is treated as material with poor warning properties, since no quantitative data are available relating warning properties to air concentrations of p-phenylene diamine.

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

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 employee).

- **Method**

At the time of publication of this guideline, no measurement method for p-phenylene diamine had been published by NIOSH.

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 minimum), and other appropriate protective clothing necessary to prevent skin contact with p-phenylene diamine or liquids containing p-phenylene diamine, where skin contact may occur.
- If employees' clothing may have become contaminated with p-phenylene diamine or liquids containing p-phenylene diamine, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with p-phenylene diamine should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of p-phenylene diamine from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-phenylene diamine, the person performing the operation should be informed of p-phenylene diamine's hazardous properties.
- Non-impervious clothing which becomes contaminated with p-phenylene diamine should be removed promptly and not reworn until the p-phenylene diamine is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where p-phenylene diamine or liquids containing p-phenylene diamine may contact the eyes.

SANITATION

- Workers subject to skin contact with p-phenylene diamine or liquids containing p-phenylene diamine should wash with soap or mild detergent and water any areas of the body which may have contacted p-phenylene diamine at the end of each work day.
- Skin that becomes contaminated with p-phenylene diamine should be promptly washed or showered with soap or mild detergent and water to remove any p-phenylene diamine.

• Eating and smoking should not be permitted in areas where p-phenylene diamine or liquids containing p-phenylene diamine are handled, processed, or stored.
• Employees who handle p-phenylene diamine or liquids containing p-phenylene diamine should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to p-phenylene diamine may occur and control methods which may be effective in each case:

Operation	Controls
Use in dye and dyestuff intermediates for fur, hair, leather, cotton, and synthetics	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in photographic application as a fine-grain developing agent, for preparation of color developers, and for photochemical measurements; use in polymer technology for manufacture of Fiber B, and as a cross-linking agent; use as a catalyst; use in preparation of epoxy resins, synthetic fibers, heat-resistant polymers, and coatings for leather, paper, and textiles	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in rubber technology for natural and synthetic rubber for vulcanization, as an antioxidant, accelerator, and stabilizer	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in organic synthesis in preparation of antioxidants for petroleum fuels; preparation of grease thickeners, electrical insulators, and rust removers	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in laboratory as an analytical reagent, and as a special solvent	General dilution ventilation; local exhaust ventilation; personal protective equipment

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 p-phenylene diamine or liquids containing p-phenylene diamine get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If p-phenylene diamine or liquids containing p-phenylene diamine get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If p-phenylene diamine or liquids containing p-phenylene diamine penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of p-phenylene diamine, 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**

When p-phenylene diamine has been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious 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 AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If p-phenylene diamine is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

p-Phenylene diamine may be disposed of:

1. By making packages of p-phenylene diamine in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving p-phenylene diamine in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR p-PHENYLENE DIAMINE

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate or Vapor Concentration	
5 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
25 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 25 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. 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.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against p-phenylene diamine. Any escape self-contained breathing apparatus.

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