Occupational Health Guideline for p-Nitroaniline

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: C₄H₄N₂O₂
- Synonyms: Azoic diazo component 37; para-nitroaniline; 4-nitroaniline; para-aminonitrobenzene; PNA; 1-amino-4-nitrobenzene; fast red 2G base; fast red GG base
- Appearance and odor: Yellow crystals with a pungent, faint, ammonia-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-nitroaniline is 1 part of p-nitroaniline per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 6 milligrams of p-nitroaniline per cubic meter of air (mg/m³).

HEALTH HAZARD INFORMATION

- Routes of exposure
- p-Nitroaniline can affect the body if it comes in contact with the skin or eyes, is inhaled, or is swallowed.
- Effects of overexposure
- 1. Short-term Exposure: p-Nitroaniline may cause a darkening or bluish coloring of the lips ("blue lip") and of the skin. Irritation of the nose and throat, headache, dizziness, weakness, nausea, shortness of breath, and rapid beating of the heart may occur. The overexposed person may become unconscious, cease breathing, and die.

- 2. Long-term Exposure: Prolonged overexposure may produce blue-colored lips and skin, and difficult breathing.
- 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 pnitroaniline.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to p-nitroaniline 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 blood, liver, and cardiovascular system should be stressed.
- —A complete blood count: p-Nitroaniline has been shown to cause methemoglobinemia. Persons with blood disorders may be at increased risk from exposure. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.
- —Liver function tests: Since liver damage has been observed in humans exposed to p-nitroaniline, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.
- 2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis. Methemoglobin determinations should be performed if overexposure is suspected or signs and symptoms of toxicity occur.
- Summary of toxicology
- p-Nitroaniline absorption, whether from inhalation of the vapor or absorption of the solid through skin, causes anoxia due to the formation of methemoglobin; jaundice and anemia have been reported. Signs and symptoms of overexposure are due to the loss of oxygen-carrying capacity of the blood. Rapid absorption through the

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.

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intact skin is frequently the main route of entry. The onset of symptoms of methemoglobinemia is often insidious and may be delayed for up to 4 hours; headache is commonly the first symptom and may become quite intense as the severity of methemoglobinemia progresses. Cyanosis develops early in the course of intoxication, first in the lips, nose, and ear lobes, and is usually recognized by fellow workers. Cyanosis occurs when the methemoglobin concentration is 15% or more. The individual usually feels well, has no complaints, and is insistent that nothing is wrong until the methemoglobin concentration approaches approximately 40%. At concentrations of over 40% there usually is weakness and dizziness; up to a 70% concentration there may be ataxia, dyspnea on mild exertion, tachycardia, nausea, vomiting, and drowsiness. Ingestion of alcohol aggravates the toxic effects of p-nitroaniline. The substance is mildly irritating to the eyes and may cause some corneal damage.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data
 - 1. Molecular weight: 138
 - 2. Boiling point (760 mm Hg): 336 C (637 F)
 - 3. Specific gravity (water = 1): 1.437
- 4. Vapor density (air = 1 at boiling point of p-nitroaniline): 4.76
 - 5. Melting point: 146 C (293 F)
 - 6. Vapor pressure at 20 C (68 F): 0.00015 mm Hg
- 7. Solubility in water, g/100 g water at 18.5 C (65 F): 0.08 (slight)
 - 8. Evaporation rate (butyl acetate = 1): 22.6
- Reactivity
 - 1. Conditions contributing to instability: Heat
- 2. Incompatibilities: Strong oxidizers and moisture may result in spontaneous heating.
- 3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide and carbon monoxide) may be released in a fire involving p-nitroaniline.
- 4. Special precautions: Liquid p-nitroaniline will attack some forms of plastics, coatings, and rubber.
- Flammability
 - 1. Flash point: 199 C (390 F) (closed cup)
 - 2. Autoignition temperature: 180 C (356 F)
- 3. Flammable limits in air, % by volume: Data not available
- 4. Extinguishant: Dry chemical and carbon dioxide for small fires.
- Warning properties
- 1. Odor Threshold: The Manufacturing Chemists Association (MCA) states that p-nitroaniline is odorless.
- 2. Eye Irritation Level: p-Nitroaniline, according to the MCA, "is mildly irritating to the eyes and may cause some corneal damage." For the purposes of this guideline, quarter- and half-facepiece respirators are allowed up to 60 mg/m³ (PF—10).
- 3. Evaluation of Warning Properties: Since the MCA states that p-nitroaniline is odorless and is only mildly

irritating to the eyes, it is treated as a material with poor warning properties. The concentration in saturated air at 20 C could result in a significant exposure relative to the permissible exposure.

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

An analytical method for p-nitroaniline is in the NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

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 repeated or prolonged skin contact with solid p-nitroaniline or liquids containing p-nitroaniline.
- If employees' clothing may have become contaminated with solid p-nitroaniline, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with p-nitroaniline should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of p-nitroaniline from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the p-nitroaniline, the person performing the operation should be informed of p-nitroaniline's hazardous properties.

- Where exposure of an employee's body to solid pnitroaniline or liquids containing p-nitroaniline may occur, 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 p-nitroaniline should be removed immediately and not reworn until the p-nitroaniline is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid p-nitroaniline or liquids containing p-nitroaniline may contact the eyes.

SANITATION

- Skin that becomes contaminated with p-nitroaniline should be immediately washed or showered with soap or mild detergent and water to remove any p-nitroaniline.
- Workers subject to skin contact with solid p-nitroaniline should wash any areas of the body which may have contacted p-nitroaniline at the end of each work day.
- Eating and smoking should not be permitted in areas where solid p-nitroaniline is handled, processed, or stored.
- Employees who handle solid p-nitroaniline or liquids containing p-nitroaniline 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-nitroaniline may occur and control methods which may be effective in each case:

Operation

Liberation during use in synthesis and subsequent product preparation, such as grinding, containerization, etc.

Controls

Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection

Operation

Liberation during production of pphenylenediamine; during production of intermediates for dyestuff manufacture; during antioxidation and antiozonation operations in rubber manufacture

Liberation during use as a gasoline-gum inhibitor; during use as an intermediate in pharmaceutical synthesis

Controls

Process enclosure; local exhaust ventilation; butyl rubber protective clothing; medical supervision; work force rotation; whole-body protection

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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-nitroaniline or liquids containing p-nitroaniline get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

Skin Exposure

If p-nitroaniline or liquids containing p-nitroaniline get on the skin, immediately flush the contaminated skin with water. If p-nitroaniline or liquids containing p-nitroaniline soak through the clothing, remove the clothing immediately and flush the skin with water. If solid p-nitroaniline penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention as soon as possible.

Breathing

If a person breathes in large amounts of p-nitroaniline, 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-nitroaniline has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

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• 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-nitroaniline 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-Nitroaniline may be disposed of:
- 1. By making packages of p-nitroaniline 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-nitroaniline 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-NITROANILINE

Condition	Minimum Respiratory Protection* Required Above 1 ppm
Particulate and Vapor Concentration	
60 mg/m³ (10 ppm) or less	Any supplied-air respirator.
	Any self-contained breathing apparatus.
300 mg/m³ (50 ppm) or less	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 300 mg/m³ (50 ppm) 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 organic vapors and particulates.
	Any escape self-contained breathing apparatus.

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

