Occupational Health Guideline for Thiram

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: $C_6H_{12}N_2S_4$
- Synonyms: Tetramethylthiuram disulfide
- Appearance: Colorless to cream solid (some commercial products are dyed blue).

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for thiram is 5 milligrams of thiram per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Thiram 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**

Thiram can cause irritation of the eyes, nose, throat, and skin. It may cause an allergic skin rash. Thiram is thought to have similar effects as antabuse which include nausea, vomiting, diarrhea, and loss of appetite. After ingestion of alcohol, individuals taking antabuse may experience skin redness, hives, itching, pulsating headache, flushing, sweating, nausea, vomiting, diarrhea, weakness, dizziness, and difficulty in breathing. Thiram has caused birth defects in offspring of animals given large doses of thiram by mouth.

- **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 thiram.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to thiram at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from thiram exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of thiram might cause exacerbation of symptoms due to its irritant properties.

—Skin disease: Thiram is a skin sensitizer. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Thiram (tetramethylthiuram disulfide) dust irritates the respiratory tract, eyes, and skin, and causes sensitization dermatitis. Thiram was teratogenic (skeletal malformations) in hamsters given a single oral dose of 250 mg/kg during the period of organogenesis and in mice given oral doses of 5 to 30 mg/animal daily between days 6 and 17 of pregnancy. In exposed humans, sensitization dermatitis in the form of eczema has occurred on the hands, forearms, and feet. Thiram is thought to have similar toxic effects to antabuse, which include nausea, vomiting, diarrhea, and loss of appetite. Ingestion of ethanol by persons taking antabuse has caused a severe reaction characterized by a rapid skin response of a non-allergic nature, flushing, erythema, pruritis, urticaria, headache, nausea, vomiting, diarrhea, weakness, dizziness, and difficult breathing.

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

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 240
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 1.40
  4. Vapor density (air = 1 at boiling point of thiram): Not applicable
  5. Melting point: 140 C (284 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong acids or oxidizable materials may cause formation of toxic gases such as hydrogen sulfide.
  3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur dioxide, carbon disulfide, and carbon monoxide) may be released in a fire involving thiram.
  4. Special precautions: None
- **Flammability**
  1. Flash point: 89 C (192 F) (closed cup)
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Carbon dioxide, foam, dry chemical
- **Warning properties**

Warning properties are not considered since the vapor pressure is negligible.

Grant states that "as a dust or spray it is irritating to the eyes . . . ." No quantitative information is available concerning the eye irritation threshold, however.

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**

Sampling and analyses may be performed by collection of thiram on a membrane filter with subsequent chemical treatment and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure thiram may be used. An analytical method for thiram is in the *NIOSH Manual of Analytical Methods.* 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

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

SANITATION

- Skin that becomes contaminated with thiram should be promptly washed or showered with soap or mild detergent and water to remove any thiram.
- Eating and smoking should not be permitted in areas where thiram is handled, processed, or stored.

• Employees who handle thiram or liquids containing thiram 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 thiram may occur and control methods which may be effective in each case:

Operation	Controls
Use in rubber industry as an accelerator, peptizing agent, and vulcanizing agent	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during application as an agricultural fungicide as foliage spray for plants and trees, fruits and seeds	Handle mechanically; personal protective equipment
Use as a bacteriostat in commercial and surgical soap, antiseptics, sunburn oils and fats	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use as an animal repellant on plants or trees	Handle mechanically; 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 thiram or liquids containing thiram 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 thiram or liquids containing thiram get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If thiram or liquids containing thiram penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Swallowing**

When thiram or liquids containing thiram have been swallowed and the person is conscious, 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.

SPILL AND DISPOSAL PROCEDURES

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

• If thiram 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:

Thiram may be disposed of:

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

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Thiram (Tetramethyl Thiuram Disulfide)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.

• Council on Pharmacy and Chemistry: "A.M.A. Outlines of Information on Pesticides, Part I – Agricultural Fungicides," *Journal of the American Medical Association*, 157:237-239 1955.

• Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.

• 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.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

• Robens, J. F.: "Teratologic Studies of Carbaryl, Diazinon, Norea, Disulfiram, and Thiram in Small Laboratory Animals," *Toxicology and Applied Pharmacology*, 15:152-163, 1969.

• Roll, R.: "Teratologische Untersuchungen mit

Thiram (TMTD) an zwei Mausestammen," *Archiv fur Toxikologie,* 27:173-186, 1971.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

• Shelley, W. B.: "Golf-Course Dermatitis Due to Thiram Fungicide," *Journal of the American Medical Association,* 188:415-417, 1964.

• Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.

RESPIRATORY PROTECTION FOR THIRAM

Condition	Minimum Respiratory Protection* Required Above 5 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any supplied-air respirator. Any self-contained breathing apparatus. Any pesticide chemical cartridge respirator.
250 mg/m³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. Any pesticide chin-style cartridge respirator with a full facepiece. A chin-style or a front- or back-mounted pesticide gas mask.
1500 mg/m³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. 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. A powered air-purifying pesticide respirator with a full facepiece, helmet, or hood.
Greater than 1500 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 dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

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