OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BISMUTH TELLURIDE DOPED WITH SELENIUM SULFIDE

INTRODUCTION

This guideline summarizes pertinent information about doped bismuth telluride for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

Bi_2Te_3 doped with Bi_2Se_3, SnTe, and Te

- **Synonyms**

Doped bismuth sesquitelluride, doped bismuth tritelluride, doped dibismuth tritelluride, doped tellurobismuthite

- **Identifiers**

1. CAS No.: 1304-82-1
2. RTECS No.: EB3110000
3. DOT UN: None
4. DOT label: None

- **Appearance and odor**

Bismuth telluride doped with selenium is a nonflammable, gray, crystalline solid that has been enhanced (or doped) with a small amount of a selenium compound; doping confers on the semiconductor the charge characteristics of the doping agent, which alters the conductivity of the semiconductor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 800.76
2. Boiling point: Data not available
3. Specific gravity (water = 1): 7.7 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 573°C (1,063.4°F)
6. Vapor pressure: Not applicable
7. Solubility: Insoluble in water; decomposes in nitric acid
8. Evaporation rate: Not applicable

- **Reactivity**

1. Conditions contributing to instability: None reported
2. Incompatibilities: A violent reaction may result from contact of doped bismuth telluride with strong oxidizers (such as bromine, fluorine, or chlorine), and a toxic gas may evolve from contact with moisture.
3. Hazardous decomposition products: Toxic materials (such as tellurium) may be released in a fire involving doped bismuth telluride.
4. Special precautions: None reported

- **Flammability**

The National Fire Protection Association has not assigned a flammability rating to doped bismuth telluride; this substance is not flammable.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use an extinguishant suitable for the materials involved in the surrounding fire.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving doped bismuth telluride.

EXPOSURE LIMITS

• **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for bismuth telluride doped with selenium sulfide is 5 mg/m^3 of air as an 8-hr time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1-A].

• **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established an 8-hr TWA of 5 mg/m^3 as the recommended exposure limit (REL) for bismuth telluride doped with selenium sulfide [NIOSH 1992].

• **ACGIH TLV®**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned bismuth telluride doped with selenium sulfide a threshold limit value (TLV) of 5 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1991b].

• **Rationale for limits**

The limits are based on the risk of respiratory effects associated with exposure to doped bismuth telluride.

HEALTH HAZARD INFORMATION

• **Routes of exposure**

Exposure to doped bismuth telluride can occur through inhalation, eye or skin contact, and ingestion.

• **Summary of toxicology**

1. *Effects on Animals*: Selenium-doped bismuth telluride causes reversible, nonfibrotic lesions in the lungs of exposed experimental animals [Clayton and Clayton 1981]. Dogs, rabbits, and rats were exposed to 15 mg/m^3 of a dust (average particle size 1.04 microns) containing a mixture of doped bismuth telluride and stannous telluride for 6 hr/day, 5 days/week for 1 year. The dogs and rabbits developed small granulomatous lesions in the lungs, and the rats developed epithelialization of the alveolar walls [ACGIH 1991a; Clayton and Clayton 1981]. Fibrotic changes did not occur in any species; in dogs examined 4 months after the cessation of exposure, these lesions had regressed, indicating reversibility [ACGIH 1991a; Clayton and Clayton 1981].

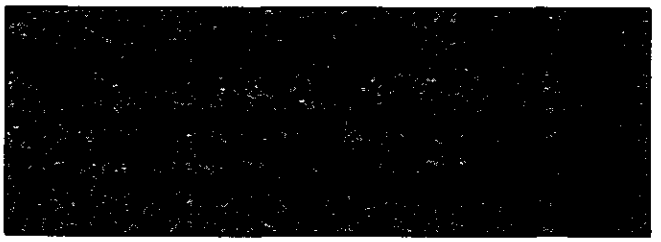
2. *Effects on Humans*: No adverse effects of exposure to doped bismuth telluride have been noted in humans except for the development of "tellurium breath" (breath that smells like garlic) [Clayton and Clayton 1981]. Based on effects seen in animals, overexposure to the dust of doped bismuth telluride is likely to cause reversible pulmonary changes in humans [Proctor et al. 1988].

• **Signs and symptoms of exposure**

1. *Acute exposure*: Acute exposure to doped bismuth telluride can cause garlic breath and local irritation of the eyes and skin.

2. *Chronic exposure*: No signs or symptoms of chronic exposure to doped bismuth telluride have been reported in humans.

• **Emergency procedures**



Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Initiate the following emergency procedures:

1. *Eye exposure*: Irritation may result! ***Immediately and thoroughly*** flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.

2. *Skin exposure*: Irritation may result. ***Immediately and thoroughly*** wash contaminated skin with soap and water.

3. *Inhalation exposure*: Move the victim to fresh air ***immediately***.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: If a large amount of doped bismuth telluride is ingested take the following steps:

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water.

—Have the victim drink a glass (8 oz) of fluid such as water.

—Induce vomiting by giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.

—Do *not* force an unconscious or convulsing person to drink fluid or to vomit.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

Use of doped bismuth telluride as a semiconductor may result in worker exposures to this substance.

The following methods are effective in controlling worker exposures to doped bismuth telluride, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

2. Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

3. Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.

4. Wadden RA, Scheff PA [1987]. Engineering design for control of workplace hazards. New York, NY: McGraw-Hill.

5. Plog BA [1988]. Fundamentals of industrial hygiene. Chicago, IL: National Safety Council.

MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to doped bismuth telluride, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to doped bismuth telluride at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with respiratory system diseases.

• Periodic medical examinations and biological monitoring

Occupational health interviews and physical examinations should be performed at regular intervals during the employ-

ment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to doped bismuth telluride exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of doped bismuth telluride on the respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for doped bismuth telluride.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and the selected physiologic or laboratory tests conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne selenium-doped bismuth telluride (measured as bismuth) is determined by using a mixed cellulose ester filter (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1989] and in the OSHA Computerized Information System [OSHA 1990].

PERSONAL HYGIENE

If the dust of doped bismuth telluride collects on the skin, workers should wash the affected areas with soap and water.

Clothing contaminated with doped bismuth telluride should be removed.

A worker who handles doped bismuth telluride should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where doped bismuth telluride is handled, processed, or stored.

STORAGE

Doped bismuth telluride should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of doped bismuth telluride should be protected from physical damage and should be stored separately from strong oxidizers, heat, sparks, and open flame. Because containers that formerly contained doped bismuth telluride may still hold product residues, they should be handled appropriately.

SPILLS

In the event of a spill involving doped bismuth telluride, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill:

1. Do not touch the spilled material.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate the area of the spill or leak.
5. Use a clean shovel and place the material into a clean, dry container; cover and remove the container from the spill area.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- **Emergency planning requirements**

Doped bismuth telluride is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

- **Reportable quantity requirements for hazardous releases**

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of doped bismuth telluride; there is no reportable quantity for this substance.

- **Community right-to-know requirements**

Employers are not required by Section 313 of SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of doped bismuth telluride emitted or released from their facility annually.

- **Hazardous waste management requirements**

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although doped bismuth telluride is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- **Conditions for respirator use**

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of doped bismuth telluride exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- **Respiratory protection program**

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective gloves and clothing should be worn to prevent skin contact with doped bismuth telluride. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use. No reports have been published on the resistance of various protective clothing materials to doped bismuth telluride permeation. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to doped bismuth telluride.

If doped bismuth telluride is dissolved in an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which doped bismuth telluride might contact the eyes (e.g., through dust particles). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with doped bismuth telluride.

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