Occupational Health Guideline for Organic Tin Compounds (as Tin)

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.

APPLICABILITY

The general guidelines contained in this document apply to all organic tin compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Dibutyltin di-2-ethylhexoate

Formula: (C₄H₉)₂Sn(C₈H₁₅O₂₊
 Synonyms: Dibutyltin dioctoate

Appearance and odor: Waxy solid with a weak odor.

Bis(tri-n-butyltin) oxide

• Formula: ((C₄H₉)₃Sn)₂O

Synonyms: TBTO

• Appearance and odor: Colorless to yellow liquid

with a weak odor.

Triphenyltin chloride

Formula: (C₆H₅)₃SnCl
Synonyms: None

• Appearance and odor: Colorless to yellow solid with

a characteristic odor.

Dibutyltin dichloride

• Formula: (C₄H₉)₂SnCl₂

Synonyms: None

 Appearance: Light tan or colorless solid or semisolid.

Dibutyltin diacetate

• Formula: (C₄H₉)₂Sn(C₂H₃O₂)₂

Synonyms: None

• Appearance and odor: Colorless liquid with a weak vinegar odor.

TetrabutyItin

• Formula: (C₄H₉)₄Sn

• Synonyms: Tetra-n-butyltin

Appearance and odor: Colorless liquid with a distinct, characteristic odor.

Stannous 2-ethylhexoate

• Formula: Sn(C₅H₁₅O₂)₂

• Synonyms: Stannous octoate; tin octoate

• Appearance and odor: Pale yellow, viscous liquid with a characteristic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for organic tin compounds is 0.1 milligram of organic tin compounds (as tin) per cubic meter of air (mg/m³) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 0.1 milligram of tin per cubic meter of air averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Organotin Compounds should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

Routes of exposure

Organic tin compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin.

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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They can also affect the body if they are swallowed and they may be absorbed through the skin.

• Effects of overexposure

Little is known of the toxicity of monoalkyl tin compounds except that the toxicity of monoethyl tin chloride is low. Dialkyl tin compounds have caused irritation of the skin and damage to the liver and bile ducts in animals. This has resulted in animal deaths from liver failure and peritonitis. Swallowing diethyl tin has caused permanent damage to the nervous system and deaths in humans. Trialkyl and tetraalkyl tin compounds have caused nervous system damage in animals. Trialkyl and dibutyl tins have caused skin burns in humans. Tetramethyl and tetraethyl tin have caused headache and vomiting in humans. Tributyl tin compounds have caused severe skin burns in humans.

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 organic tin compounds.

Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to organic tin compounds 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 central nervous system, eyes, liver, and urinary tract should be stressed. The skin should be examined for evidence of chronic disorders.
- —Urinalysis: Since some organic tin compounds may cause urinary retention, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.
- —Liver function tests: Organic tin compounds cause hepatic necrosis in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.
- —A complete blood count: Organic tin compounds cause hemolysis in animals. A complete blood count should be performed including a red cell count, a white cell count, a differential on a stained smear, as well as hemoglobin and hematocrit.
- —Eye disease: Since some organic tin compounds may produce neurological damage, the eyes should be examined for such abnormalities as glaucoma and choked disc; general tests of visual acuity should be performed as well. In addition, evidence indicating past or present increased intracranial pressure should be evaluated.
- —Cardiovascular system: An electrocardiogram should be performed on workers over 40 years of age and where indicated.
- —Skin disease: Organic tin compounds are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

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

Summary of toxicology

The organic tin compounds, chiefly solids and liquids, cause irritation of the eyes, throat, and skin; some produce cerebral edema, while others cause hepatic necrosis. Oral administration of a preparation of organic tin containing diethyltin di-iodide and up to 10% triethyltin for treatment of human furunculosis resulted in 217 cases of poisoning, 100 of which were fatal. After a latent period of 4 days there was severe persistent headache followed by vertigo, visual disturbances including photophobia, abdominal pain, vomiting, and urinary retention; the more severe cases showed transient or permanent paralysis and psychic disturbances. Residual symptoms in those who recovered included persistent headache, diminished visual acuity, partial paresis, focal anesthesia, and in four severe cases, flaccid paraplegia with incontinence. The most significant lesion found at necropsy was cerebral edema. Repeated oral administration to rats of 50 mg/kg of dibutyltin chloride resulted in inflammation of bile ducts and hepatic necrosis; repeated skin applications of 10 mg/kg caused severe local skin injury and bile duct damage. Triethyltin sulfate administered repeatedly to rats at 10 mg/kg caused tremors and paresis, which in some animals progressed to complete paralysis and death; it was equally toxic by mouth and by injection. In mice, tributyltin chloride had a marked hemolytic action, while dibutyl and tetrabutyl tin were less markedly hemolytic. Workers exposed to the vapor or fume of butyltin compounds developed sore throat and cough several hours after exposure. Chemical burns from organic tin compounds may result from only brief contact with the skin; pain is usually moderate and itching is the chief symptom; healing is usually complete within 7 to 10 days. When a worker was splashed in the face with a tributyltin compound, lacrimation and severe conjunctivitis appeared within minutes, despite immediate lavage, and persisted for 4 days; at the end of 7 days the eyes appeared normal.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data—Dibutyltin di-2-ethylhexoate
 - 1. Molecular weight: 522.7
 - 2. Boiling point (760 mm Hg): Decomposes
 - 3. Specific gravity (water = 1): 1.07
- 4. Vapor density (air = 1 at boiling point of dibutyltin di-2-ethylhexoate): Not applicable
 - 5. Melting point: 54 C (129 F)
 - 6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
- 7. Solubility in water, g/100 g water at 20 C (68 F):
- 8. Evaporation rate (butyl acetate = 1): Not applicable
- Physical data—Bis(tri-n-butyltin) oxide
 - 1. Molecular weight: 595.4

- 2. Boiling point (760 mm Hg): 254 C (489 F) at 50 mm Hg
 - 3. Specific gravity (water = 1): 1.17
- 4. Vapor density (air = 1 at boiling point of bis(tri-n-butyltin)oxide): Not applicable
 - 5. Melting point: Data not available
- 6. Vapor pressure at 20 C (68 F): Much less than 1 nm Hg
- 7. Solubility in water, g/100 g water at 20 C (68 F): Less than 20 ppm
- 8. Evaporation rate (butyl acetate = 1): Not applicable

Physical data—Triphenyltin chloride

- 1. Molecular weight: 385.5
- 2. Boiling point (760 mm Hg): 240 C (464 F) at 13 mm Hg
 - 3. Specific gravity (water = 1): Greater than 1
- 4. Vapor density (air = 1 at boiling point of triphenyltin chloride): Not applicable
 - 5. Melting point: 106 C (223 F)
 - 6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
- 7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
- 8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data-Dibutyltin dichloride

- 1. Molecular weight: 303.8
- 2. Boiling point (760 mm Hg): 135 C (275 F) at 10 mm Hg
 - 3. Specific gravity (water = 1): 1.36
- 4. Vapor density (air = 1 at boiling point of dibutyltin dichloride): Not applicable
 - 5. Melting point: 43 C (109 F)
- 6. Vapor pressure at 20 C (68 F): 2 mm Hg/100 C (212 F)
- 7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
- 8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Dibutltin diacetate

- 1. Molecular weight: 351
- 2. Boiling point (760 mm Hg): 144 C (291 F) at 10 mm Hg
 - 3. Specific gravity (water = 1): 1.32
- 4. Vapor density (air = 1 at boiling point of dibutyltin diacetate): Not applicable
 - 5. Melting point: 10 C (50 F)
 - 6. Vapor pressure at 20 C (68 F): 1.3 mm Hg
- 7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
- 8. Evaporation rate (butyl acetate = 1): Not applicable

Physical data—Tetrabutyltin

- 1. Molecular weight: 347.2
- 2. Boiling point (760 mm Hg): 145 C (293 F) at 10 mm Hg
 - 3. Specific gravity (water = 1): 1.06
- 4. Vapor density (air = 1 at boiling point of tetrabutyltin): Not applicable

- 5. Melting point: Less than 70 C (less than 94 F)
- 6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
- 7. Solubility in water, g/100 g water at 20 C (68 F): Slight
- 8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Stannous 2-ethylhexoate

- 1. Molecular weight: 404.7
- 2. Boiling point (760 mm Hg): Decomposes at 200 C (392 F)
 - 3. Specific gravity (water = 1): 1.26
- 4. Vapor density (air = 1 at boiling point of stannous 2-ethylhexoate): Not applicable
 - 5. Melting point: Less than -25 C (less than -13 F)
 - 6. Vapor pressure at 20 C (68 F): Less than 1 mm Hg
- 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.
- 3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving organic tin compounds.
- 4. Special precautions: Organic tin compounds will attack some forms of plastics, rubber, and coatings.

Flammability

- 1. Flash point: a) Dibutyltin di-2-ethylhexoate: Data not available; b) Bis(tri-n-butyltin) oxide: Greater than 100 C (212 F); c) Triphenyltin chloride: Data not available; d) Dibutyltin dichloride: 168 C (334 F); e) Dibutyltin diacetate: 143 C (289 F); f) Tetrabutyltin: 124 C (255 F); g) Stannous 2-ethylhexoate: 142 C (287 F)
 - 2. Autoignition temperature: Data not available
- 3. Flammable limits in air, % by volume: Data not available (probably because too high boiling points)
- 4. Extinguishant: Water, foam, dry chemical, and carbon dioxide

Warning properties

Concerning the toxicity of organic tin, Browning states "The eyes are rarely involved, but accidental splashing can cause lacrimation and intense suffusion of the conjunctiva which persists for several days, but with no permanent injury."

Grant lists several toxic effects produced by triethyltin on the eye, but these injuries are caused by systemic poisoning, not by a local effect on the eye.

The NIOSH Criteria Document cites Landa et al. as having observed eye and upper respiratory tract irritation from bis(tributyltin) oxide at an average air concentration of 0.05 mg/m³ measured as tin, but noted that this concentration may not be entirely accurate since the limit of sensitivity of the measurement method used was 0.1 mg/m³.

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 organic tin compounds on a filter, followed by chemical treatment and subsequent spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure organic tin compounds may be used. An analytical method for organic tin compounds is in the NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 1, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00267-3).

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 any possibility of skin contact with triphenyltin chloride or liquids containing triphenyltin chloride.
- 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 dibutyltin di-2-ethylhexoate or liquids containing dibutyltin di-2-ethylhexoate, liquid bis(tri-n-butyltin) oxide, solid or liquid dibutyltin diacetate, liquid tetrabutyltin, or liquid stannous 2-ethylhexoate.
- 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 dibutyltin dichloride or liquids containing dibutyltin dichloride, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with solid triphenyltin chloride or dibutyltin dichloride, employees should change into uncontaminated clothing before leaving the work premises
- If employees' clothing may have become contaminated with solid dibutyltin di-2-ethylhexoate, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to triphenyltin chloride or liquids containing triphenyltin chloride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Where exposure of an employee's body to dibutyltin dichloride or liquids containing dibutyltin dichloride 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 triphenyltin chloride or dibutyltin dichloride should be removed immediately and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of triphenyltin chloride or liquids containing triphenyltin chloride contacting the eyes.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where dibutyltin di-2-ethylhexoate or liquids containing dibutyltin di-2-ethylhexoate, dibutyltin dichloride or liquids contain-

ing dibutyltin dichloride, liquid bis(tri-n-butyltin) oxide, solid or liquid dibutyltin diacetate, liquid tetrabutyltin, or liquid stannous 2-ethylhexoate may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to triphenyltin chloride or liquids containing triphenyltin chloride, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with triphenyltin chloride or dibutyltin dichloride should be immediately flushed with large amounts of water to remove any contaminant.
- Workers subject to skin contact with solid dibutyltin di-2-ethylhexoate, triphenyltin chloride, or dibutyltin dichloride should wash with soap or mild detergent and water any areas of the body which may have contacted any contaminant at the end of each work day.
- Skin that becomes contaminated with dibutyltin di-2ethylhexoate, bis(tri-n-butyltin) oxide, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.
- Eating and smoking should not be permitted in areas where dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, dibutyltin dichloride, dibutyltin diacetate, or tetrabutyltin are handled, processed, or stored.
- Employees who handle dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate 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 organic tin compounds may occur and control methods which may be effective in each case:

Operation

Use as a stabilizing agent against degradation effects fo light, heat, and oxygen on poly vinyl chloride, neoprene, chlorinated polyethylenes, vinyl copolymers, silicones, and polyamides

Controls

Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation

Use as a catalyst in organic and inorganic synthesis in condensation, esterification, halogenation, hydrogenation, oxidation, and polymerization

Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Controls

Use in manufacture of insecticides, bactericides, fungicides, and molluscides; use as U.S. Food and Drugsanctioned chemical on agricultural crops

Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Use in manufacture of rodent repellants for wire cable

Local exhaust ventilation; general dilution ventilation; personal protective equipment

Use as veterinary medicine as poultry anthelmintic

General dilution ventilation

Use as a fuel additive and lubricant

Process enclosure

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 organic tin compounds 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 these chemicals.

Skin Exposure

If dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate get on the skin, immediately flush with large amounts of water, then wash with soap or mild detergent and water. If dibutyltin di-2-ethylhexoate, bis(tri-n-butyltin) oxide, triphenyltin chloride, dibutyltin dichloride, dibutyltin diacetate, tetrabutyltin, or stannous 2-ethylhexoate soak through the clothing, remove the clothing immediately and flush with large amounts of water and then wash using soap or mild detergent and water. Get medical attention immediately.

• Breathing

If a person breathes in large amounts of organic tin compounds, 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 organic tin compounds 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.

• 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 organic tin compounds are spilled or leaked, the following steps should be taken:
- 1. Ventilate area of spill or leak.
- 2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing organic tin compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.
- Waste disposal method:

Organic tin compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR ORGANIC TIN COMPOUNDS (AS TIN)

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m³
Particulate Concentration	
1 mg/m³ or less	A chemical cartridge respirator with an organic vapor cartridge(s) and a dust and mist filter.
	Any supplied-air respirator.
	Any self-contained breathing apparatus.
5 mg/m³ or less	Any chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and high efficiency filter (s).
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
50 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 50 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 organic vapors and particulates.
	Any escape self-contained breathing apparatus.

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