OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR tert-BUTYL CHROMATE

INTRODUCTION

This guideline summarizes pertinent information about tert-butyl chromate (measured as chromate) 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 Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- **Formula**

  $C_8H_{18}CrO_4$

- **Structure**

  $[(CH_3)_3CO]_2CrO_2$

- **Synonyms**

  t-Butyl chromate; bis(tert-butyl)chromate; chromic acid, di-tert-butyl ester.

- **Identifiers**

  1. CAS No.: 1189-85-1
  2. RTECS No.: GB2900000
  3. DOT UN: None
  4. DOT label: None

- **Appearance and odor**

  tert-Butyl chromate is a clear, colorless liquid.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

  1. Molecular weight: 230.3
  2. Boiling point: Data not available
  3. Specific gravity: Data not available
  4. Vapor density (air = 1 at boiling point of tert-butyl chromate): 7.9
  5. Melting point: -5° to 0°C (23° to 32°F)
  6. Vapor pressure: Data not available
  7. Solubility: tert-Butyl chromate is miscible with water
  8. Evaporation rate: Data not available

- **Reactivity**

  1. Conditions contributing to instability: Heat, sparks, and open flame may ignite the flammable liquid solution used as a carrier for shipping tert-butyl chromate.

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2. Incompatibilities: Contact of tert-butyl chromate with reducing agents and moisture should be avoided, and contact with acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur) may cause a violent reaction.

3. Hazardous decomposition products: Acrid and irritating fumes and poisonous gases may be released in a fire involving tert-butyl chromate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to tert-butyl chromate. Other sources rate tert-butyl chromate as a dangerous fire hazard.

1. Flash point: Data not available

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, sand, water spray, or foam to extinguish fires involving tert-butyl chromate.

Fires involving tert-butyl chromate should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas. Vapor explosion and poison hazards may occur indoors, outdoors, or in sewers. Vapors may travel to a source of ignition and flash back. Containers of tert-butyl chromate may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if a rising sound from a venting safety device is heard or if there is discoloration of a container due to fire. Dikes should be used to contain fire-control water for later disposal. If a tank car or truck is involved in a fire, personnel should isolate an area of a half mile in all directions. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving tert-butyl chromate. Structural fire-fighters' protective clothing will provide limited protection against fires involving tert-butyl chromate.

EXPOSURE LIMITS

- **OSHA PEL**

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for tert-butyl chromate (measured as chromate) is 0.1 mg/m^3 as a ceiling limit. A worker's exposure to tert-butyl chromate shall at no time exceed this ceiling level. The OSHA PEL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [29 CFR 1910.1000, Table Z-1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) considers tert-butyl chromate a potential human carcinogen and has issued a recommended exposure limit (REL) for tert-butyl chromate (measured as hexavalent chromium) of 1 g/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned tert-butyl chromate (measured as chromate) a ceiling limit value of 0.1 mg/m^3, which should not be exceeded during any part of the working exposure. The ACGIH also assigns a "Skin" notation to tert-butyl chromate [ACGIH 1993].

- **Rationale for limits**

The NIOSH limit is based on the inferred risk of cancer associated with exposure to this substance [NIOSH 1992]. The ACGIH limit is based on the risk of pulmonary changes, narcosis, and necrotic lesions of the skin associated with exposure to this substance [ACGIH 1991].

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to tert-butyl chromate can occur through

inhalation, ingestion, eye or skin contact, and absorption through the skin.

- **Summary of toxicology**

1. *Effects on Animals:* tert-Butyl chromate is a hexavalent chromium compound. Although there are no acute toxicity data specifically for this chromate, hexavalent chromium compounds are known to cause cancer in experimental animals, including lung cancers, injection-site tumors, and cancer of the kidneys [Langard 1988]. In contact with the skin of animals, tert-butyl chromate causes necrosis of the skin at the site of contact; death caused by percutaneous absorption of lethal quantities of this substance also occurs [ACGIH 1991]. Rats exposed repeatedly for 30 to 60 minutes/day to an unspecified but lethal concentration of tert-butyl chromate and butyl alcohol showed signs of respiratory and skin irritation and behavioral changes before death [ACGIH 1991]. At autopsy, lung edema and fatty deposition in the liver were seen in these animals [ACGIH 1991]. In another study, exposure of rats to tert-butyl chromate alone (concentration not specified) caused an increase in respiratory rate and signs of mild narcosis [ACGIH 1991].

2. *Effects on Humans:* NIOSH classifies all hexavalent chromium compounds, including tert-butyl chromate, as potential occupational carcinogens. However, there is little toxicity information specifically for organic hexavalent compounds, including tert-butyl chromate. In humans, tert-butyl chromate causes acid-like burns and necrotic lesions in contact with the eyes or skin, and exposure to the vapor of this substance causes irritation of the upper respiratory tract and may lead to ulceration of the nasal septum [NJDH 1987]. Skin contact can also cause an allergic rash in sensitive individuals, and long-term exposure may lead to kidney or liver damage [NJDH 1987].

- **Signs and symptoms of exposure**

1. *Acute exposure:* The signs and symptoms of acute exposure to tert-butyl chromate include redness and inflammation of the eyes and eyelids, runny nose, sore throat, coughing, nose bleeds, nasal discharge, crusting or sores in the nose, and skin and eye burns.

2. *Chronic exposure:* The signs and symptoms of chronic exposure to tert-butyl chromate include perforation of the nasal septum, jaundice, enlarged and tender liver, and blood, pus, or protein in the urine.

- **Emergency procedures**

> **WARNING!**
>
> **Transport victims immediately to emergency medical facility!**

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. ***Immediately*** initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of tert-butyl chromate! ***Immediately but gently*** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! ***Immediately*** remove all contaminated clothing! ***Immediately, continuously, and gently*** wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. *Inhalation exposure:* Move the victim to fresh air ***immediately.*** Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

   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:* Take the following steps if tert-butyl chromate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cav-

ity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and ***no more***.

—Do ***not*** permit the victim to drink milk or carbonated beverages!

—Do ***not*** permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

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, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve tert-butyl chromate and lead to worker exposures to this substance:

—Use in specialty reactions as an organic source of chromium

—Manufacture of catalysts

—Use for polymerizing olefins and as a curing agent for urethane resins

The following methods are effective in controlling worker exposures to tert-butyl chromate, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information on control methods are as follows:

1. ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 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 that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, 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 tert-butyl chromate, 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 concen-

trate on the function and integrity of the eyes, skin, respiratory tract, kidneys, and liver. 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 medical conditions that may be aggravated or may result in increased risk when a worker is exposed to tert-butyl chromate 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 of skin or respiratory allergies or findings consistent with diseases of the eyes, skin, respiratory tract, kidneys, or liver.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment 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 tert-butyl chromate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of tert-butyl chromate on the eyes, skin, respiratory tract, kidney, or liver. 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. Urinary chromium concentrations correlate well with airborne chromium concentrations and are believed to be good indicators of recent short-term exposure. A urinary chromium level of 40-50 g/liter urine, or 30 g per gram creatinine, is believed to correspond to exposure to an airborne chromium level of 0.05 mg/m3 [Baselt 1988].

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

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population. Because occupational exposure to tert-butyl chromate may cause diseases with prolonged latent periods, the need for medical monitoring may extend well beyond the termination of employment.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne tert-butyl chromate is made using a low ash polyvinyl chloride (LAPVC) 5-micron filter. Samples are collected at a maximum flow rate of 2.0 liters/min until a maximum air volume of 960 liters is collected. The sample is then treated with a carbonate/bicarbonate buffer to extract the tert-butyl chromate. Analysis is conducted by polarographic analysis using differential pulse polarography. This method has a sampling and analytical error of 0.18 and is described in the OSHA Computerized Information System [OSHA 1993] and in Method ID-103 of the *OSHA Analytical Methods Manual* [OSHA 1985].

PERSONAL HYGIENE

Because tert-butyl chromate can be absorbed through the skin in toxic amounts, workers should immediately wash any affected areas with soap and water.

Clothing contaminated with tert-butyl chromate should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of tert-butyl chromate, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles tert-butyl chromate should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where tert-butyl chromate or a solution containing tert-butyl chromate is handled, processed, or stored.

STORAGE

tert-Butyl chromate should be stored in an explosion-proof refrigerator in tightly sealed containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred; inside storage should be in a standard flammable liquids storage room. Containers of tert-butyl chromate should be protected from physical damage and should be stored separately from reducing agents, moisture, acids, alcohols, and combustible organic or easily oxidized materials (such as paper, wood, plastic, aluminum, and sulfur), heat, sparks, and open flame. Because containers that formerly contained tert-butyl chromate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving tert-butyl chromate, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.

2. Remove all sources of heat and ignition.

3. Water spray may be used to reduce vapors, but the spray may not prevent ignition in closed spaces.

4. For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.

5. For large liquid spills, build dikes far ahead of the spill to contain the tert-butyl chromate for later reclamation or disposal.

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**

  tert-Butyl chromate 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 tert-butyl chromate; there is no reportable quantity for this substance.

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

  Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and that manufacture 25,000 lb or more or otherwise use 10,000 lb or more of a chromium compound per calendar year are required by EPA [40 CFR 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of such compounds 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 tert-butyl chromate 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 any 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 addi-

tion, 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 tert-butyl chromate 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, respirator 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 about the selection and use of respirators and about 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 clothing should be worn to prevent any skin contact with tert-butyl chromate. 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 tert-butyl chromate permeation; however, butyl rubber and polyvinyl chloride have been tested against a chemically similar material (chromic acid) and will potentially resist permeation for periods greater than 4 but fewer than 8 hours. Since specific test data are not available for tert-butyl chromate, the information provided here should be considered as a guideline only. 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 tert-butyl chromate.

Safety glasses, goggles, or face shields should be worn during operations in which tert-butyl chromate might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with tert-butyl chromate. Contact lenses should not be worn if the potential exists for tert-butyl chromate exposure.

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