OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR DICROTOPHOS

INTRODUCTION

This guideline summarizes pertinent information about dicrotophos 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 Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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

C₈H₁₆NO₅P

Structure

• Synonyms

Bidrin; phosphoric acid, dimethyl ester; ester with (E)-3-hydroxy-N,N-dimethylcrotonamide; Bidirl; Carbicron; Ektafos; Oleobidrin; 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl phosphate (E)-isomer; dimethyl 1-dimethylcarbonyl-1-propen-2-yl phosphate

Identifiers

1. CAS No.: 141-66-2

2. RTECS No.: TC3850000

3. DOT NA: 2783 55

4. DOT label: Poison

· Appearance and odor

Dicrotophos is a yellow-brown liquid with a mild ester odor. Eighty-five percent of the commercial grade consists of the E-isomer, which is amber in color and more insecticidally active than the Z-isomer.

CHEMICAL AND PHYSICAL PROPERTIES

· Physical data

1. Molecular weight: 237.21

2. Boiling point (760 mm Hg): 400°C (752°F)

3. Specific gravity (water = 1): 1.22 at 15° C (59°F)

4. Vapor density: Data not available

5. Melting point: Data not available

6. Vapor pressure at 20°C (68°F): 0.0001 mm Hg

Solubility: Miscible with water, methylene chloride, ethanol, isopropyl and diacetone alcohols, acetoni-

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trile, and xylene; slightly soluble in kerosene and diesel fuel.

8. Evaporation rate: Data not available

Reactivity

- 1. Conditions contributing to instability: Heat, sparks, and open flame
- 2. Incompatibilities: None reported.
- Hazardous decomposition products: Toxic gases (such as oxides of phosphorus and nitrogen) may be released in a fire involving dicrotophos.
- Special precautions: Dicrotophos is somewhat corrosive to cast iron, mild steel, brass, and stainless steel 304.

Flammability

The National Fire Protection Association has not assigned a fire hazard rating to dicrotophos.

- 1. Flash point: Greater than 93°C (200°F) (closed cup)
- 2. Autoignition temperature: Data not available
- 3. Flammable limits in air: Data not available
- Extinguishant: Use dry chemical, water spray, or standard foam to fight fires involving dicrotophos.

Fires involving dicrotophos 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 and ventilate closed spaces before entering. Containers of dicrotophos 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. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and selfcontained breathing apparatus when fighting fires involving dicrotophos. Chemical protective clothing that is specifically recommended for dicrotophos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving dicrotophos.

EXPOSURE LIMITS

OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for dicrotophos [29 CFR 1910.1000, Table Z-11.

NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.25 mg/m³ as a TWA for up to a 10-hr workday and a 40-hr workweek for dicrotophos. The NIOSH REL also bears a "Skin" notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [NIOSH 1992].

ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned dicrotophos a threshold limit value (TLV) of 0.25 mg/m³ as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH has also assigned a "Skin" notation to dicrotophos [ACGIH 1993].

Rationale for limits

The NIOSH and ACGIH limits are based on the risk of cholinesterase inhibition associated with exposure to dicrotophos.

HEALTH HAZARD INFORMATION

Routes of exposure

Exposure to dicrotophos can occur through inhalation, ingestion, and absorption through the skin.

Summary of toxicology

Effects on Animals: Dicrotophos is a highly toxic organophosphorus pesticide that causes cholinesterase inhibition in animals [EPA 1989]. The dermal LD₅₀ in rabbits is 168 mg/kg [NIOSH 1993]. The 4-hr LC₅₀ in rats is 90 mg/m³ [NIOSH 1993]. The oral LD₅₀ is 13 mg/kg in rats and 11 mg/kg in mice [NIOSH 1993]. Rats fed dicrotophos for 2 years at a dietary level of 1, 10, or 100 ppm showed no effects at the 1-ppm level

but had decreased body weights and reduced cholinesterase activity at the higher levels [ACGIH 1991]. Dogs fed 0.16, 1.6, or 16 ppm for 2 years experienced mild episodes of excessive salivation and, at the highest dose, showed depressed plasma and red blood cell cholinesterase activity [ACGIH 1991].

2. Effects on Humans: Dicrotophos is an inhibitor of plasma and red blood cell cholinesterase activity in humans. There are two reports of severe poisoning attributed to dicrotophos, one involving a 41-year-old farmer who had applied this substance to his crops and used it inside his house to control insects, and the other involving a 52-year-old man who ingested a mixture of turpentine and dicrotophos after a drinking bout [Hayes 1982]. Both of these patients eventually recovered after initially responding to treatment and then relapsing seriously [Hayes 1982].

• Signs and symptoms of exposure

- Acute exposure: The signs and symptoms of acute exposure to dicrotophos include those of cholinesterase inhibition: headache, nausea, dizziness, anxiety, restlessness, muscle twitching, weakness, tremor, incoordination, vomiting, abdominal cramps, and diarrhea; excessive salivation, sweating, tearing of the eyes, and runny nose also may occur.
- Chronic exposure: The signs and symptoms of chronic exposure to dicrotophos include persistent anorexia, weakness, and malaise, brought on by repeated absorption of dicrotophos in amounts that are not sufficient to cause acute poisoning.

Emergency Procedures

WARNING!

Exposed victims may die!

Transport 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: Immediately and thoroughly rinse concentrated solutions, vapors, mists, or aerosols of

- dicrotophos from the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.
- 2. Skin exposure: Irritation may result from exposure to concentrated solutions, vapors, mists, or aerosols of dicrotophos. Dicrotophos can be absorbed through the skin in lethal amounts! *Immediately* remove contaminated clothing and *thoroughly* wash contaminated skin with soap and water for at least 15 min.
- Inhalation exposure: If vapors, mists, or aerosols of dicrotophos are inhaled, move the victim to fresh air immediately.

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

- 4. Ingestion exposure: Take the following steps if dicrotophos or any material containing it is ingested:
 - —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 having the victim touch the back of the throat with a finger until productive vomiting ceases. Do not give syrup of ipecac because of possible onset of respiratory depression and seizures.
 - —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

The following operations may involve dicrotophos and lead to worker exposures to this substance:

—Manufacture, formulation, and application of dicrotophos-containing insecticides and acaricides to cotton, apples, grains, vegetables, ornamentals, shrubs, trees, and other crops

The following methods that are effective in controlling worker exposures to dicrotophos, 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:

- ACGIH [1992]. Industrial ventilation—a manual of recommended practice. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- Burton DJ [1986]. Industrial ventilation—a self study companion. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
- Alden JL, Kane JM [1982]. Design of industrial ventilation systems. New York, NY: Industrial Press, Inc.
- 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 dicrotophos, the 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 blood. A pre-exposure red blood cell and plasma cholinesterase activity baseline should also be established.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to dicrotophos 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 reduced plasma or red blood cell cholinesterase activity.

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 dicrotophos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of dicrotophos on red blood cell and plasma cholinesterase activity. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

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Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophorus compounds such as dicrotophos. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for dicrotophos (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70 percent of the individual's pre-exposure baseline. The same method and laboratory should be used for pre-exposure and exposure measurements to reduce variability.

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 a patient who has recovered from the acute phase of organophosphorus poisoning remains hypersusceptible to anticholinesterases for as long as several weeks or months, the need for medical monitoring may extend well beyond the acute poisoning episode.

WORKPLACE MONITORING AND MEASUREMENT

Determination of a worker's exposure to airborne dicrotophos is made using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD-2 tube (270/140 mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a recommended flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. The sample is then treated with toluene to extract the dicrotophos. Analysis is conducted by gas chromatography using a flame photometric detector. This method is included in the OSHA Laboratory In-House Methods File [1989].

PERSONAL HYGIENE

Dicrotophos can be absorbed through the skin in toxic amounts. Therefore, if dicrotophos contacts the skin, workers should immediately and repeatedly wash the body (including hair, scalp, and nails) with soap and water. Get medical help immediately.

Clothing contaminated with dicrotophos 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 dicrotophos, particularly its potential to be absorbed through the skin in toxic amounts.

A worker who handles dicrotophos 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 dicrotophos or a solution containing dicrotophos is handled, processed, or stored.

STORAGE

Dicrotophos 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]. Storage areas must be located at a suitable distance from inhabited buildings, animal shelters, and food stores and must be inaccessible to unauthorized persons. Containers of dicrotophos should be protected from physical damage, heat, sparks, and open flame. Dicrotophos decomposes when stored at temperatures about 25°C to 30°C (77°F to 86°F). Containers should be stacked in a manner that permits free circulation of air at the bottom and insides of the stacks of containers.

SPILLS AND LEAKS

In the event of a spill or leak involving dicrotophos, 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. Notify safety personnel.
- 3. Remove all sources of heat and ignition.
- 4. Ventilate the area of the spill or leak.
- Use water spray to reduce vapors; do not get water inside the container.

- 6. For small dry spills, use a clean shovel and gently place the material into a clean, dry container, creating as little dust as possible; cover and remove the container from the spill area.
- For small liquid spills, take up with sand or other noncombustible absorbent material and place into closed containers for later disposal.
- For large liquid spills, build dikes far ahead of the spill to contain the dicrotophos 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

Employers owning or operating a facility at which there are 100 lb or more of dicrotophos must comply with EPA's emergency planning requirements [40 CFR 355.40].

Reportable quantity requirements for hazardous releases

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for dicrotophos is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center immediately at (800) 424-8802 or at (202) 426-2675 in Washington, D.C. [40 CFR 302.6].

- —Notify the State emergency response commission of any State likely to be affected by the release [40 CFR 355.40].
- —Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

Community right-to-know requirements

Employers are not required by Section 313 of the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of dicrotophos 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 dicrotophos 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 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

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the use of respirators to control exposure. Respirators must be worn if the ambient concentration of dicrotophos 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 (gloves, full-body covering, and head protection) should be worn as appropriate to prevent any possibility of skin contact with dicrotophos. 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 dicrotophos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have shown that material made of a laminate of Vitron/neoprene or butyl rubber/neoprene provides good protection against permeation by this group of substances. Since specific test data are not available for dicrotophos, 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 dicrotophos.

If dicrotophos 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 dicrotophos 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 dicrotophos.

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