OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CRUFOMATE

INTRODUCTION

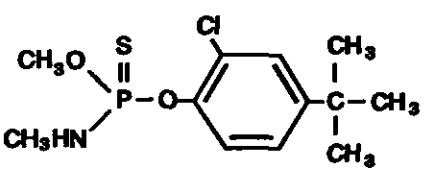
This guideline summarizes pertinent information about crufomate for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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

$C_{12}H_{19}ClNO_3P$

- **Structure**



- **Synonyms**

Amidofos; 4-tert-butyl-2-chlorophenyl methyl methylphosphoramidate; Dowco 132; Montrel; o-methyl-o-2-chloro-4-tert-butylphenyl N-methylamidophosphate; Ruelene

- **Identifiers**

1. CAS No.: 299-86-5
2. RTECS No.: TB3850000
3. DOT UN: 2765 55 (phenoxy pesticides, solid, toxic, n.o.s.)
4. DOT label: Poison or St. Andrew's Cross (depending on quantity shipped)

- **Appearance and odor**

Crufomate is a white, crystalline solid in pure form; the commercial product is a yellow oil. Crufomate is an organophosphorus pesticide.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data

1. Molecular weight: 291.7
2. Boiling point (0.01 mm Hg): 117° to 118°C (242.6° to 244.4°F)
3. Specific gravity (water = 1): 1.2 at 70°C (158°F)
4. Vapor density: Not applicable
5. Melting point: 60° to 60.5°C (140° to 141°F) (pure); 58.7°C (137.7°F) (92%, technical grade)

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
Education and Information Division

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

6. Vapor pressure at 117°C (242.6°F): 0.01 mm Hg

7. Solubility: Practically insoluble in water and light petroleum; soluble in benzene, alcohol, ethyl ether, cyclohexane, carbon tetrachloride, and acetonitrile.

8. Evaporation rate: Not applicable

Reactivity

1. Conditions contributing to instability: Heat, sparks, open flame, strong alkalies, and strong acids. Crufomate is unstable over long periods of time, in water preparations, and at temperatures above 60°C (140°F).

2. Incompatibilities: Crufomate decomposes in strongly alkaline (greater than pH 7) and strongly acidic media.

3. Hazardous decomposition products: Toxic gases (such as oxides of phosphorus and nitrogen, and chlorine) may be released in a fire involving crufomate.

4. Special precautions: None reported

Flammability

The National Fire Protection Association has not assigned a flammability rating to crufomate.

1. Flash point: 41.1° to 60°C (106° to 140°F), depending on the formulation

2. Autoignition temperature: Data not available

3. Flammable limits in air: Data not available

4. Extinguishant: Use dry chemical, water spray, or standard foam for small fires. Water spray, fog, or standard foam is recommended to fight large fires involving crufomate.

Fires involving crufomate 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 crufomate 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 self-contained breathing apparatus when fighting fires involving crufomate. Chemical protective clothing that is specifically recommended for crufomate may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving crufomate.

EXPOSURE LIMITS

- **OSHA PEL**

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for crufomate [29 CFR 1910.1000, Table Z- 1].

- **NIOSH REL**

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 5 mg/m^3 as a TWA for up to a 10-hr workday and a 40-hr workweek and 20 mg/m^3 as a 15-min short-term exposure limit (STEL). A STEL is a 15-min TWA concentration that should not be exceeded at any time during a workday [NIOSH 1992a].

- **ACGIH TLV**

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned crufomate 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 1993].

- **Rationale for limits**

The NIOSH limit is based on the risk of neurotoxicity and cholinesterase inhibition. The ACGIH limit is based on the risk of cholinesterase inhibition associated with exposure to crufomate.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Exposure to crufomate can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**

1. *Effects on Animals:* In animals, crufomate is an inhibitor of plasma and erythrocyte cholinesterase.

Application of crufomate to the eye of rabbits as undiluted or 10% solutions resulted in corneal cloudiness and conjunctival irritation, along with slight pain [Clayton and Clayton 1982; ACGIH 1991]. Crufomate produced slight erythema when applied undiluted or as a 10% solution to the abraded or intact skin of the rabbit [Clayton and Clayton 1982; ACGIH 1991]. The dermal LD_{50} in rabbits is 2,000 mg/kg [NIOSH 1992b]. The lowest toxic inhalation dose in rats is 12 mg/m^3 for 4 hr [NIOSH 1992b]. The oral LD_{50} is 460 mg/kg in rats, 400 mg/kg in rabbits, and 1,000 mg/kg in guinea pigs [NIOSH 1992b]. Dogs fed 250 ppm crufomate in the diet for 75 days exhibited depression of blood cholinesterase and slight liver morphological changes; no effects were observed in dogs given dietary doses of 40 or 125 ppm [Clayton and Clayton 1982]. In 90-day dietary studies in rats, blood and/or brain cholinesterase levels were depressed 40% to 60% as compared with levels in untreated controls when doses of 30 to 1,000 ppm (1.5 to 50 mg/kg/day) were administered; no other adverse effects were observed in these animals [Clayton and Clayton 1982]. Rats fed 1,000 ppm (50 mg/kg/day) for 2 years showed marked cholinesterase inhibition, growth retardation, atrophy of the muscles of the hind limbs, and slight degeneration of the sciatic nerve; after 12, 18, or 24 months on this regimen, there was a 50% reduction in testes weights, reflecting degeneration and atrophy of the seminiferous tubules [Clayton and Clayton 1982]. No teratologic or reproductive effects were seen in male and female rats fed up to 500 ppm crufomate (25 mg/kg/day) for three generations [Clayton and Clayton 1982]. In female mice treated dermally with 50 or 100 mg/kg crufomate on days 35 and 21 before mating, the lower dose prolonged the gestation period and decreased the index of lactation and the higher dose reduced conception rate, litter size, and lactation index and decreased fetal body weight [NLM 1992].

2. *Effects on Humans:* In humans, crufomate is a moderately potent cholinesterase inhibitor.

- **Signs and symptoms of exposure**

1. *Acute exposure:* Acute overexposure to crufomate by the oral route may cause severe gastrointestinal effects such as cramps, diarrhea, nausea, and anorexia. Acute inhalation exposure can cause wheezing, difficult breathing, blurred vision, and tearing. Dermal exposure causes localized twitching and sweating. Severe overexposure by any route can cause respiratory paralysis, coma, and death.

2. *Chronic exposure:* Continued low-level exposure to crufomate may lead to acetylcholine buildup, causing the signs and symptoms of systemic poisoning described above for acute overexposure.

- **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! ***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 and skin corrosion 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 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 crufomate or any material containing it is ingested:

   —Do ***not*** induce vomiting.

   —Have the victim rinse the contaminated mouth cavity 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 can sometimes 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 and the location and proper use of emergency equipment.

EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve crufomate and may result in worker exposures to this substance:

—Manufacture of crufomate and crufomate-containing pesticides

—Formulation and application of crufomate and crufomate-containing pesticides

—Use as a selective insecticide against cattle grubs, horn flies, and lice

The following methods are effective in controlling worker exposures to crufomate, 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 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 crufomate, 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 blood. A pre-exposure plasma and red blood cell 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 crufomate 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 and red blood cell cholinesterase activity levels.

- **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 crufomate exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of crufomate on the levels of plasma or red blood cell 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.

  Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. Absorption of crufomate can be confirmed by analysis of urine for its metabolite, crufomate phenol. However, correlations between airborne and urinary levels of crufomate and its metabolite have not been established. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as crufomate. RBC ChE is an indicator both of acute and chronic overexposure. The recommended biological index for crufomate (and other organophosphorus compounds) is an RBC ChE activity level that is at least 70% 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. 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 crufomate is determined by 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 recommended air volume of 120 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method is described in OSHA's Laboratory In-House Methods File [OSHA 1989].

PERSONAL HYGIENE

If crufomate contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with crufomate should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering the clothes should be informed of the hazardous properties of crufomate.

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

STORAGE

Crufomate 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]. Crufomate is unstable over long periods of time in water preparations and at temperatures above 60°C (140°F). Containers of crufomate must be stacked in a manner that permits free circulation of air below and inside the pile of containers. Containers of crufomate should be protected from physical damage and should be stored separately from strong acids, strong alkalies, heat, sparks, and open flame. Because containers that formerly contained crufomate may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving crufomate, 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 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. Water spray may be used to reduce vapors.
5. 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.
6. For small liquid spills, absorb with sand or other noncombustible absorbent material and place into closed containers for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the crufomate 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**

  Crufomate 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 crufomate; 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 crufomate 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 crufomate is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [42 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 crufomate 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 pro-

tection 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 crufomate. 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 crufomate permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated some resistance to permeation by these compounds: a laminate of Viton and neoprene, or a laminate of butyl rubber and neoprene. Since specific test data are not available for crufomate, 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 crufomate.

If crufomate is dissolved 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 crufomate 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 crufomate.

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