# OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CHLORPYRIFOS

# INTRODUCTION

This guideline summarizes pertinent information about chlorpyrifos 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 Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether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<sub>9</sub>H<sub>11</sub>Cl<sub>3</sub>NO<sub>3</sub>PS

Structure

Synonyms

Brodan; chloropyrifos-ethyl; O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate; DOWCO 179; Dursban; Lorsban; Pyrinex

Identifiers

1. CAS No.: 2921-88-2

2. RTECS No.: TF6300000

3. DOT UN: 2783 55

4. DOT label: None

Appearance and odor

Chlorpyrifos is a colorless to white, crystalline solid with a mild, mercaptan-like odor. The technical grade often contains volatile contaminants, which are partly responsible for the offensive odor of this substance. Chlorpyrifos is an organophosphate insecticide.

# **CHEMICAL AND PHYSICAL PROPERTIES**

· Physical data

1. Molecular weight: 350.57

2. Boiling point (760 mm Hg): Data not available

3. Specific gravity (water = 1): 1.398 at 43.5°C (110.3°F) (liquid)

4. Vapor density: Data not available

5. Melting point: 41° to 42°C (105.8° to 107.6°F)

6. Vapor pressure at 25°C (77°F): 0.00002 mm Hg

 Solubility: Slightly soluble in water; soluble in most organic solvents; slowly hydrolyzed by acid or alkaline solutions

8. Evaporation rate: Data not available

## 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

## Reactivity

- Conditions contributing to instability: Heat, sparks, and open flame
- Incompatibilities: Contact of chlorpyrifos with strong acids (such as hydrochloric, sulfuric, or nitric acid) causes a violent reaction. Contact with acidic or alkaline solutions causes hydrolysis.
- Hazardous decomposition products: Toxic gases (such as chlorine and the oxides of nitrogen, phosphorus, and sulfur) may be released in a fire involving chlorpyrifos.
- Special precautions: Chlorpyrifos is corrosive to copper and brass.

#### - Flammability

The National Fire Protection Association has not assigned a flammability rating to chlorpyrifos; however, this substance is combustible.

- Flash point: 27.8°C (82°F)(Dursban®); 30.6°C (87°F)(Lorsban)(TAG 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 chlorpyrifos.

Fires involving chlorpyrifos 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 chlorpyrifos may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Do not scatter this material. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorpyrifos. Chemical protective clothing that is specifically recommended for chlorpyrifos may not provide thermal protection unless so stated by the clothing manufacturer. Structural firefighters' protective clothing is not effective against fires involving chlorpyrifos.

#### **EXPOSURE LIMITS**

#### OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for chlorpyrifos [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 0.2 mg/m³ as a TWA for up to a 10-hr workday and a 40-hr workweek and 0.6 mg/m³ as a short-term exposure limit (STEL). The STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday. 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 chlorpyrifos a threshold limit value (TLV) of 0.2 mg/m<sup>3</sup> as a TWA for a normal 8-hr workday and a 40-hr workweek. The ACGIH also assigns a "Skin" notation to chlorpyrifos [ACGIH 1993].

### · Rationale for limits

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

### **HEALTH HAZARD INFORMATION**

# · Routes of exposure

Exposure to chlorpyrifos can occur through inhalation, ingestion, eye or skin contact, and absorption through the skin.

# Summary of toxicology

 Effects on Animals: In animals, chlorpyrifos is an inhibitor of blood and plasma cholinesterase. The dermal LD<sub>50</sub> in rabbits is 2,000 mg/kg, and the oral LD<sub>50</sub> in rats is 82 mg/kg [NIOSH 1990]. Administered to monkeys at doses of 2.0 or 0.4 mg/kg/day for

- 6 months (route not specified), chlorpyrifos caused inhibition of plasma and red blood cell cholinesterase; at a dose of 0.08 mg/kg/day, only the plasma enzyme was inhibited in these animals [Hayes 1982]. Brain cholinesterase was not affected at any of these doses, and no clinical or morphological effects were noted at autopsy [Hayes 1982]. In 2-year feeding studies in dogs and rats, doses of 1 or 3 mg/kg/day produced depression of plasma and red blood cell cholinesterase; brain cholinesterase was depressed only at the highest dose [Hayes 1982]. In both rats and dogs, even the highest dose (3 mg/kg/day) produced no clinically important effects, as judged by survival, growth, relative and absolute organ weights, blood, urine, and clinical chemical findings, and gross and microscopic pathology [Hayes 1982]. In a three-generation reproduction and fertility study, no teratologic or reproductive effects were seen in male and female rats fed 1 mg/kg/day chlorpyrifos [ACGIH 1991].
- 2. Effects on Humans: In humans, chlorpyrifos is an inhibitor of plasma cholinesterase. The lowest toxic dose in humans is estimated to be 300 mg/kg; this dose caused peripheral nervous system effects, muscular weakness, and coma [NIOSH 1990]. Four repeated chlorpyrifos doses (10 mg/kg each) were applied to the skin of volunteers for a 24-hr period application) and caused no plasma (each cholinesterase depression; however, increasing the dose to 25 mg/kg did produce plasma cholinesterase inhibition, even when the duration of skin contact was reduced to 12 hr [ACGIH 1991]. Human male volunteers given 0.014 or 0.03-mg/kg chlorpyrifos per day for 20 days, followed by 0.1 mg/kg/day for an additional 9 days, showed no adverse behavioral effects or changes in hematology, urinalysis, or biochemistry parameters [Hayes 1982]. At the highest dose, plasma cholinesterase was depressed in these volunteers, but cholinesterase levels returned to normal within 4 weeks of the cessation of exposure. Red blood cell cholinesterase activity was not affected at any level [Hayes 1982]. Five of seven workers applying chlorpyrifos spray with hand-operated power sprayers (0.5% emulsion or 0.25% or 0.5% suspensions of water-wettable powder) had plasma cholinesterase values that were more than 50% below baseline values within 2 weeks after beginning work, and one worker had a plasma enzyme reduction that was greater than 70%. No inhibition of red blood cell cholinesterase was observed in these workers, and there were no signs or symptoms of illness [Hayes 1982; ACGIH 1991].

#### Signs and symptoms of exposure

- 1. Acute exposure: Acute exposure to chlorpyrifos depends on the route and extent of exposure. Inhalation can cause respiratory and ocular effects, often within a few minutes of exposure, and may cause a feeling of tightness in the chest, wheezing, laryngeal spasms, excessive salivation, bluish/purplish discoloration of the skin and lips, narrowed pupils, blurred vision, tearing, runny nose, or frontal headache. Ingestion of chlorpyrifos may cause anorexia, nausea, vomiting, abdominal cramps, and diarrhea. Skin absorption may result in localized sweating and muscle tremors in the area where skin absorption took place.
- 2. Chronic exposure: Repeated exposure to concentrations of chlorpyrifos too low to cause signs or symptoms after a single exposure may produce the signs and symptoms of poisoning described above. Continued daily exposure to low doses of chlorpyrifos may cause increasingly severe effects.

## · Emergency procedures

#### WARNING!

Seek immediate medical attention for severely affected victims or for victims with signs and symptoms of toxicity or irritation!

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

- Eye exposure: Irritation may result. Immediately and thoroughly flush the eyes with large amounts of water, occasionally lifting the upper and lower eyelids.
- Skin exposure: Skin irritation or absorption of toxic amounts may result. *Immediately* remove contaminated clothing and *thoroughly* wash contaminated skin with soap and water.
- 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 con-

tamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

- 4. Ingestion exposure: Take the following steps if chlorpyrifos 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 giving syrup of ipecac as directed on the package. If ipecac is unavailable, have the victim touch the back of the throat with a finger until productive vomiting ceases.
  - —Do not force an unconscious or convulsing person to drink fluid or to vomit.
- 5. Rescue: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

# EXPOSURE SOURCES AND CONTROL METHODS

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

- Manufacture, formulation, and application of pesticides containing chlorpyrifos
- -Use as an acaricide
- —Use as an agricultural insecticide on corn, deciduous fruits and nuts, alfalfa, cotton, sorghum, and citrus crops and as a nonagricultural pesticide for household pests and aquatic larvae
- —Use in controlling chinch bugs in Gulf Coast states and in controlling ticks on cattle and sheep in Australia

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

- ACGIH [1992]. Industrial ventilation—a manual of recommended practice. 21st ed. 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.
- 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 chlorpyrifos, a licensed health care professional should evaluate and document the worker's base-

line 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 (plasma and red blood cell cholinesterase levels).

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 chlorpyrifos 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 diseases of the blood. Pre-exposure baseline plasma and red blood cell cholinesterase levels should be established.

# 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 chlorpyrifos exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorpyrifos on plasma or red blood cell cholinesterase activity levels. 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. The measurement of red blood cell cholinesterase (RBC ChE) is a nonspecific and qualitative indicator of exposure to organophosphorus compounds such as chlorpyrifos. RBC ChE is an indicator of both acute and chronic overexposure. The recommended biological exposure index for chlorpyrifos (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 preexposure and exposure measurements to reduce variability.

# Medical examinations recommended at the time of iob 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.

# WORKPLACE MONITORING AND MEASUREMENT

A worker's exposure to airborne chlorpyrifos is determined by using an OSHA Versatile Sampler (OVS-2) with a 13-mm XAD tube (270/140-mg sections, 20/60 mesh) with glass fiber filter enclosed. Samples are collected at a maximum flow rate of 1.0 liter/min until a maximum air volume of 480 liters is collected. Analysis is conducted by gas chromatography using a flame photometric detector. This method has a sampling and analytical error of 0.05 and is found in OSHA Method No. 62 in the OSHA Analytical Methods Manual [OSHA 1985].

#### PERSONAL HYGIENE

If chlorpyrifos contacts the skin, workers should immediately wash the affected areas with soap and water.

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

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

# **STORAGE**

Chlorpyrifos should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accor-

dance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of chlorpyrifos should be protected from physical damage and should be stored separately from strong acids (such as hydrochloric, sulfuric, or nitric acid), heat, sparks, and open flame. Because containers that formerly contained chlorpyrifos may still hold product residues, they should be handled appropriately.

# **SPILLS AND LEAKS**

In the event of a spill or leak involving chlorpyrifos, 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. Ventilate the area of the spill or leak.
- 5. Use water spray to reduce vapors.
- 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, absorb 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 chlorpyrifos 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

Chlorpyrifos 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

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 contaminated 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 authorities.

The reportable quantity for chlorpyrifos 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 emergency response commission of the 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 SARA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of chlorpyrifos 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 chlorpyrifos 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 chlorpyrifos 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 only use 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 chlorpyrifos. 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 chlorpyrifos permeation; however, the following materials have been tested against chemically similar materials (organophosphorus compounds) and have demonstrated good resistance: laminates of Viton and neoprene or of butyl rubber and neoprene. Since specific test data are not available for chlorpyrifos, 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 chlorpyrifos.

If chlorpyrifos is dissolved in water or 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 chlorpyrifos might contact the eyes (e.g., through dust particles or 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 chlorpyrifos. Contact lenses should not be worn if the potential exists for chlorpyrifos exposure.

#### REFERENCES CITED

ACGIH [1991]. Documentation of the threshold limit values and biological exposure indices. 6th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

ACGIH [1993]. 1993-1994 Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

CFR. Code of Federal regulations. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

Hayes WJ, Jr. [1982]. Pesticides studied in man. Baltimore, MD: Williams & Wilkins.

NIOSH [1987a]. NIOSH guide to industrial respiratory protection. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-116.

NIOSH [1987b]. NIOSH respirator decision logic. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-108.

NIOSH [1990]. Registry of toxic effects of chemical substances database: chlorpyrifos. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health

Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Standards Development and Technology Transfer, Technical Information Branch.

NIOSH [1992]. NIOSH recommendations for occupational safety and health: compendium of policy documents and statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

OSHA [1985]. OSHA analytical methods manual. Salt Lake City, UT: U.S. Department of Labor, Occupational Safety and Heath Administration, OSHA Analytical Laboratory.