

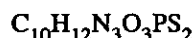
OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR AZINPHOS-METHYL

INTRODUCTION

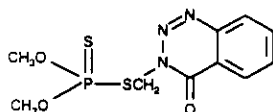
This guideline summarizes pertinent information about azinphos-methyl for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information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

SUBSTANCE IDENTIFICATION

• Formula



• Structure



• Synonyms

Guthion; methyl guthion; benzotriazine derivative of methyl dithiophosphate; benzotriazine-dithiophosphoric acid, dimethoxy ester; O-O-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl-methyl] phosphoro-dithioate; Bay 9027; Bayer 9027; Carfene; Cotnion methyl; Gusathion

• Identifiers

1. CAS No.: 86-50-0
2. RTECS No.: TE1925000
3. DOT UN: 2783 55
4. DOT label: Poison

• Appearance and odor

Azinphos-methyl is an organophosphorus pesticide. The technical product is a brown waxy solid; no data are available regarding the odor of this substance.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 317.34
2. Boiling point (at 760 mm Hg): Decomposes at temperatures above 200°C (392°F)
3. Specific gravity (water = 1): 1.44 at 20°C (68°F)
4. Vapor density: Not applicable
5. Melting point: 73° to 74°C (163.4° to 165.2°F)
6. Vapor pressure at 20°C (68°F): 0.00038 mm Hg
7. Solubility: Slightly soluble in water; soluble in methanol, ethanol, propylene glycol, xylene, and other organic solvents
8. Evaporation rate: Negligible

• Reactivity

1. Conditions contributing to instability: Heat, sparks, or flame.
2. Incompatibilities: Fires and explosions may result from contact of azinphos-methyl with strong oxidizers.
3. Hazardous decomposition products: Toxic gases and dusts (such as oxides of nitrogen, phosphorus, and sulfur) may be released when azinphos-methyl is heated to decomposition.
4. Special precautions: None

• Flammability

The National Fire Protection Association has not assigned a flammability rating to azinphos-methyl; this substance may burn, but it does not ignite readily.

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, carbon dioxide, Halon[®], water spray, or standard foam to fight small fires involving

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azinphos-methyl; use water spray, fog, or standard foam to fight large fires involving this substance.

Fires involving azinphos-methyl should be fought upwind and 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 azinphos-methyl 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 they hear a rising sound from a venting safety device or if a container becomes discolored as a result of 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 (including a self-contained breathing apparatus) when fighting fires involving azinphos-methyl. Chemical protective clothing that is specifically recommended for azinphos-methyl may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters' protective clothing may not provide protection against permeation by azinphos-methyl.

EXPOSURE LIMITS

• OSHA PEL

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for azinphos-methyl is 0.2 mg/m^3 of air as an 8-hr time-weighted average (TWA). 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-A].

• NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.2 mg/m^3 as an 8-hr TWA with a "Skin" notation [NIOSH 1992].

• ACGIH TLV®

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned azinphos-methyl a threshold limit value (TLV) of 0.2 mg/m^3 as a TWA for a normal 8-hr workday and a 40-hr workweek; the TLV also bears a "Skin" notation [ACGIH 1991b].

• Rationale for limits

The limits are based on the risk of anticholinesterase effects associated with exposure to azinphos-methyl.

HEALTH HAZARD INFORMATION

• Routes of exposure

Exposure to azinphos-methyl can occur through inhalation, ingestion, skin absorption, and eye or skin contact.

• Summary of toxicology

1. *Effects on Animals:* Azinphos-methyl is a cholinesterase inhibitor in animals that is capable of inducing death from respiratory arrest. Significant dermal absorption can occur in animals. The dermal LD_{50} is about 65 mg/kg in mice and 220 mg/kg in rats [NIOSH 1991]. Among rats that inhaled an aerosol of technical grade product containing 72% to 73% azinphos-methyl, the 1-hr LC_{50} was approximately 75 mg/m^3 (69 mg/m^3 for males and 79 mg/m^3 for females). The signs and symptoms of toxic cholinesterase inhibition included salivation, lacrimation, exophthalmos, defecation, urination, and muscle fasciculations before respiratory failure and death [NIOSH 1991; SRI 1978]. The oral LD_{50} was 15 mg/kg in mice and 7 mg/kg in rats [NIOSH 1991]. Rats that inhaled azinphos-methyl at 4.72 mg/m^3 for 12 weeks (6 hr/day, 5 days/week) showed a significant reduction in erythrocyte and plasma cholinesterase activity [Proctor et al. 1988]. Rats tolerated a dietary concentration of 5 ppm for 60 days without cholinesterase inhibition; at 20 ppm for 60 days, however, brain and red blood cell cholinesterase levels were inhibited by as much as 30% [ACGIH 1991a]. When azinphos-methyl was administered to pregnant mice and rats, it caused no adverse developmental effects in the offspring [NIOSH 1991; NLM 1991]. A National Cancer Institute study provided equivocal evidence that oral dosing of male rats with azinphos-methyl causes cancer of the thyroid and pancreas; this substance was not shown to be carcinogenic in female rats or in male or female mice [NCI 1978].

2. *Effects on Humans:* Azinphos-methyl is a cholinesterase inhibitor in humans. Eight workers engaged in the formulation of a wettable azinphos-methyl powder were exposed to concentrations as high as 9.6 mg/m^3 ; blood serum levels in some workers were depressed to 78% of their pre-exposure baseline cholinesterase levels [Proctor et al. 1988]. In a group of male agricultural workers working in a field that had been treated with azinphos-methyl, the mean red blood cell cholinesterase activity was significantly below that of workers engaged in an untreated field [NLM 1991]. Volunteers ingesting 4 to 20 mg azinphos-methyl/day for 30 days did not show a drop in cholinesterase levels [ACGIH 1991a].

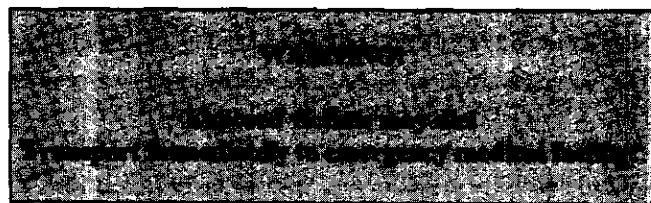
• Signs and symptoms of exposure

1. *Acute exposure:* The following signs and symptoms of acute exposure to azinphos-methyl vary with the route of entry and the degree of exposure [NLM 1991]. Effects associated with inhalation exposure include a feeling of

tightness in the chest, wheezing, bronchoconstriction, excessive bronchial secretion, laryngeal spasms, excessive salivation, cyanosis, miosis, pain in and between the eyes, blurring of distant vision, tearing, rhinorrhea, and frontal headache. Within 15 to 120 min of ingestion, gastrointestinal effects appear—anorexia, nausea, vomiting, abdominal cramps, and diarrhea. After skin absorption, sweating and muscle twitching occur in the area of skin contact. If overexposure by any route is severe, signs and symptoms include muscular weakness, involuntary twitching, and eventually paralysis. The most serious consequence is paralysis of the respiratory muscles. Effects on the central nervous system include giddiness, confusion, ataxia, slurred speech, Cheyne-Stokes respiration, convulsions, coma, and loss of reflexes. Blood pressure may fall, and cardiac irregularities (including complete heart block) may occur; these effects are sometimes reversible if adequate pulmonary ventilation is established. Unless the exposure is lethal, complete symptomatic recovery usually occurs within 1 week; however, increased susceptibility to the effects of anticholinesterase agents usually persists for several weeks after exposure.

2. *Chronic exposure:* Repeated exposure to azinphos-methyl at concentrations below those that will cause symptoms after a single exposure can cause the same signs and symptoms as acute exposure.

• Emergency procedures



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

1. *Eye exposure:* **Immediately and thoroughly** flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. *Skin exposure:* Azinphos-methyl 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.

3. *Inhalation exposure:* If particulates or vapors, mists, or aerosols of azinphos-methyl are inhaled, move the victim to fresh air **immediately**. Have the victim blow his or her nose 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 azinphos-methyl or any material containing it is ingested:

—Have the victim rinse the contaminated mouth cavity several times with a 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 involve azinphos-methyl and may result in worker exposures to this substance:

—Manufacture, formulation, and application of azinphos-methyl as an insecticide and acaricide on field crops, fruits, vegetables, cotton, tobacco, nuts, sugar cane, soybeans, ornamentals, grasses, and trees

—Use of azinphos-methyl as an additive in the food and drinking water of animals

The following methods are effective in controlling worker exposures to azinphos-methyl, 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, placement of workers in jobs that do not jeopardize their safety or health, 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 azinphos-methyl, 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 baseline red blood cell acetylcholinesterase level should be established for each potentially exposed worker.

A preplacement medical evaluation is recommended to assess an individual's suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to azinphos-methyl 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 decreases in blood 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 azinphos-methyl exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of azinphos-methyl on blood 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. Red blood cell cholinesterase activity can be measured to monitor both acute and chronic exposure to azinphos-methyl. A worker should be removed from exposure if his or her erythrocyte cholinesterase level drops to or below 40% of the pre-exposure baseline value for that individual; he or she should not be allowed to return to work until this level has again reached 80% of the pre-exposure baseline level.

• 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 job 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

Neither NIOSH nor OSHA has a validated method for sampling azinphos-methyl in the workplace. However, the following secondary analytical method, which has not been validated, is available.

A worker's exposure to airborne azinphos-methyl is determined by using a specially designed tube called an OSHA versatile sampler (OVS-2) containing XAD-2 resin (270/140-mg sections, 20/60 mesh) and a glass fiber filter. Samples are collected at a recommended flow rate of 1 liter/min until a recommended air volume of 480 liters is collected. The sample is desorbed with toluene. Analysis is conducted by gas chromatography using a flame photometric detector and an OV-1 column at 175°C (347°F). The limit

of detection for this procedure is 5 µg/sample. This method is described in the OSHA Laboratory In-House Methods File [OSHA 1991].

PERSONAL HYGIENE

Because azinphos-methyl can be deadly if absorbed through the skin, an exposed worker should remove any contaminated clothing immediately and flush the affected areas with copious amounts of water for 15 min; the worker should then wash thoroughly with soap and water. At the end of the day, workers who handle azinphos-methyl or liquid containing azinphos-methyl should use soap and water to wash any areas of the body that may have contacted this pesticide, even if none is detected on the skin.

Clothing and shoes contaminated with azinphos-methyl should be removed immediately; speed in removing these articles is essential. Persons laundering contaminated clothing should be informed of the hazardous properties of azinphos-methyl, particularly its potential for being absorbed through the skin.

A worker who handles azinphos-methyl should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where azinphos-methyl or a solution containing it is handled, processed, or stored.

STORAGE

Azinphos-methyl should be stored in a cool, dry, well-ventilated area in tightly sealed original containers that are labeled in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of azinphos-methyl should be protected from physical damage and should be separated from oxidizers, heat, sparks, and open flame. Azinphos-methyl should never be stored near any type of food. Because containers that formerly contained azinphos-methyl may still hold product residues, they should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving azinphos-methyl, 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.
2. Notify safety personnel.
3. Ventilate the atmosphere to reduce the concentration.

4. Use water spray to reduce vapors.
5. For dry spills (azinphos-methyl in solid form), use a clean shovel and place the material in a clean, dry container; cover and remove the container from the spill area.
6. Absorb small liquid spills (azinphos-methyl formulations) with sand or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the azinphos-methyl 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 with 10,000 lb or more of azinphos-methyl onsite must comply with EPA's emergency planning requirements [40 CFR 355.30]. (The employer must comply with these requirements if azinphos-methyl is in the form of a finely divided powder or is handled in solution or in molten form, and if 10 lb or more is present at the facility.)

• 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 of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). 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 azinphos-methyl 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 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 azinphos-methyl 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 azinphos-methyl 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 azinphos-methyl 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, 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 on the selection and use of respirators and on 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 possibility of skin contact with azinphos-methyl. Gloves, overalls, and boots should be worn when handling azinphos-methyl or any organophosphorus pesticide. 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. The following materials have been recommended for use against permeation by azinphos-methyl and may provide protection for periods greater than 8 hr: neoprene and nitrile rubber. Natural rubber and polyvinyl chloride have demonstrated questionable resistance to permeation by azinphos-methyl.

If azinphos-methyl 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 azinphos-methyl might contact the eyes (e.g., through dust particles, mists, 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 azinphos-methyl. Contact lenses should not be worn if the potential exists for azinphos-methyl exposure.

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