

O,O'-Diethyl dithiophosphate

sc-250605

Material Safety Data Sheet



The Power is Question

Hazard Alert Code Key: **EXTREME** **HIGH** **MODERATE** **LOW**

Section 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME

O,O'-Diethyl dithiophosphate

STATEMENT OF HAZARDOUS NATURE

CONSIDERED A HAZARDOUS SUBSTANCE ACCORDING TO OSHA 29 CFR 1910.1200.

NFPA



SUPPLIER

Company: Santa Cruz Biotechnology, Inc.

Address:

2145 Delaware Ave

Santa Cruz, CA 95060

Telephone: 800.457.3801 or 831.457.3800

Emergency Tel: CHEMWATCH: From within the US and Canada:
877-715-9305

Emergency Tel: From outside the US and Canada: +800 2436 2255
(1-800-CHEMCALL) or call +613 9573 3112

PRODUCT USE

■ Reagent. Intermediate. O,O-diethyl dithiophosphate is used as an intermediate in the production of an agricultural insecticide.

SYNONYMS

C4-H11-O2-PS2, (C₂H₅O)₂P(S)SH, "phosphorodithioic acid, O, O-diethyl ester", "phosphorodithioic acid, O, O-diethyl ester", diethyldithiophosphate, "O, O-diethyl dithiophosphate", "O, O-diethyl dithiophosphate", DEA

Section 2 - HAZARDS IDENTIFICATION

CANADIAN WHMIS SYMBOLS



EMERGENCY OVERVIEW

RISK

Causes burns.

Risk of serious damage to eyes.

Toxic by inhalation, in contact with skin and if swallowed.

Very toxic to aquatic organisms.

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POTENTIAL HEALTH EFFECTS

ACUTE HEALTH EFFECTS

SWALLOWED

- Toxic effects may result from the accidental ingestion of the material; animal experiments indicate that ingestion of less than 40 gram may be fatal or may produce serious damage to the health of the individual.
- The material can produce chemical burns within the oral cavity and gastrointestinal tract following ingestion.
- Ingestion of acidic corrosives may produce burns around and in the mouth, the throat and esophagus. Immediate pain and difficulties in swallowing and speaking may also be evident. Swelling of the epiglottis may make it difficult to breathe which may result in suffocation. More severe exposure may result in vomiting blood and thick mucus, shock, abnormally low blood pressure, fluctuating pulse, shallow respiration and clammy skin, inflammation of stomach wall, and rupture of esophageal tissue. Untreated shock may eventually result in kidney failure. Severe cases may result in perforation of the stomach and abdominal cavity with consequent infection, rigidity and fever. There may be severe narrowing of the esophageal or pyloric sphincters; this may occur immediately or after a delay of weeks to years. There may be coma and convulsions, followed by death due to infection of the abdominal cavity, kidneys or lungs.
- Thiophosphates (phosphothioate esters) do not generally produce the same degree of cholinesterase inhibition associated with other organophosphates. They may however react with a range of compounds to produce such inhibitors. Ingestion of large quantities may produce severe abdominal pains, thirst, acidaemia, difficult breathing, convulsions, collapse, shock and even death. Organophosphates may suppress the immune system in some animal species.

EYE

- The material can produce chemical burns to the eye following direct contact. Vapors or mists may be extremely irritating.
- If applied to the eyes, this material causes severe eye damage.
- Direct eye contact with acid corrosives may produce pain, tears, sensitivity to light and burns. Mild burns of the epithelia generally recover rapidly and completely. Severe burns produce long-lasting and possibly irreversible damage. The appearance of the burn may not be apparent for several weeks after the initial contact. The cornea may ultimately become deeply opaque resulting in blindness.
- Exposure to H₂S may produce pain, blurred vision, and irritation. These symptoms are temporary in all but severe cases. Eye irritation may produce conjunctivitis, photophobia, pain, and at higher concentrations blurred vision and corneal blistering.

SKIN

- Skin contact with the material may produce toxic effects; systemic effects may result following absorption.
- The material can produce chemical burns following direct contact with the skin.
- Skin contact with acidic corrosives may result in pain and burns; these may be deep with distinct edges and may heal slowly with the formation of scar tissue.
- Open cuts, abraded or irritated skin should not be exposed to this material.
- Entry into the blood-stream, through, for example, cuts, abrasions or lesions, may produce systemic injury with harmful effects. Examine the skin prior to the use of the material and ensure that any external damage is suitably protected.

INHALED

- Inhalation of aerosols (mists, fumes), generated by the material during the course of normal handling, may produce toxic effects; these may be fatal.
- The material can cause respiratory irritation in some persons. The body's response to such irritation can cause further lung damage.
- Corrosive acids can cause irritation of the respiratory tract, with coughing, choking and mucous membrane damage. There may be dizziness, headache, nausea and weakness. Swelling of the lungs can occur, either immediately or after a delay; symptoms of this include chest tightness, shortness of breath, frothy phlegm and cyanosis. Lack of oxygen can cause death hours after onset.
- Hydrogen sulfide poisoning can cause increased secretion of saliva, nausea, vomiting, diarrhea, giddiness, headache, vertigo, memory loss, palpitations, heartbeat irregularities, weakness, muscle cramps, confusion, sudden collapse, unconsciousness and death due to paralysis of breathing (at levels above 300 parts per million). The "rotten egg" odor is not a good indicator of exposure since odor fatigue occurs and odor is lost at over 200 ppm. The gas can enter the body through a punctured ear drum and even wearing some respiratory protection. Immediate supportive care is essential. Ensure medical help is addressed as part of the site emergency plan and that employees who may be accidentally exposed are made aware of the existence of such a plan.

CHRONIC HEALTH EFFECTS

- Repeated or prolonged exposure to acids may result in the erosion of teeth, swelling and or ulceration of mouth lining. Irritation of airways to lung, with cough, and inflammation of lung tissue often occurs. Chronic exposure may inflame the skin or conjunctiva. Long-term exposure to respiratory irritants may result in disease of the airways involving difficult breathing and related systemic problems. Limited evidence suggests that repeated or long-term occupational exposure may produce cumulative health effects involving organs or biochemical systems.
- Long term low level exposure to hydrogen sulfide may produce headache, fatigue, dizziness, irritability and loss of sexual desire. These symptoms may also result when exposed to hydrogen sulfide at high concentration for a short period of time.
- Alkyl thiophosphates may degrade, under certain circumstances, to produce hydrogen sulfide and alkyl mercaptans.

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

O,O'-Diethyl dithiophosphate

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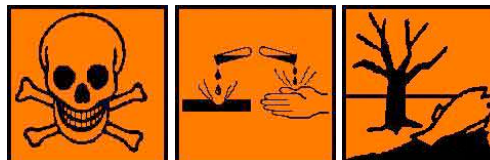
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HAZARD RATINGS

	Min	Max	
Flammability:	1		
Toxicity:	3		
Body Contact:	3		
Reactivity:	1		
Chronic:	2		
			Min/Nil=0 Low=1 Moderate=2 High=3 Extreme=4



NAME	CAS RN	%
diethyl dithiophosphate	298-06-6	>98
hydrolyses to give		
hydrogen sulfide	7783-06-4	>1

Section 4 - FIRST AID MEASURES

SWALLOWED

- For advice, contact a Poisons Information Center or a doctor at once.
- Urgent hospital treatment is likely to be needed.
- If swallowed do NOT induce vomiting.
- If vomiting occurs, lean patient forward or place on left side (head-down position, if possible) to maintain open airway and prevent aspiration.
- Observe the patient carefully.
- Never give liquid to a person showing signs of being sleepy or with reduced awareness; i.e. becoming unconscious.
- Give water to rinse out mouth, then provide liquid slowly and as much as casualty can comfortably drink.
- Transport to hospital or doctor without delay.

EYE

- If this product comes in contact with the eyes:
 - Immediately hold eyelids apart and flush the eye continuously with running water.
 - Ensure complete irrigation of the eye by keeping eyelids apart and away from eye and moving the eyelids by occasionally lifting the upper and lower lids.
 - Continue flushing until advised to stop by the Poisons Information Center or a doctor, or for at least 15 minutes.
 - Transport to hospital or doctor without delay.
 - Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

SKIN

- If skin or hair contact occurs:
 - Immediately flush body and clothes with large amounts of water, using safety shower if available.
 - Quickly remove all contaminated clothing, including footwear.
 - Wash skin and hair with running water. Continue flushing with water until advised to stop by the Poisons Information Center.
 - Transport to hospital, or doctor.

INHALED

- If fumes or combustion products are inhaled remove from contaminated area.
- Lay patient down. Keep warm and rested.
- Prostheses such as false teeth, which may block airway, should be removed, where possible, prior to initiating first aid procedures.
- Apply artificial respiration if not breathing, preferably with a demand valve resuscitator, bag-valve mask device, or pocket mask as trained. Perform CPR if necessary.
- Transport to hospital, or doctor, without delay.

Inhalation of vapors or aerosols (mists, fumes) may cause lung edema. Corrosive substances may cause lung damage (e.g. lung edema, fluid in the lungs). As this reaction may be delayed up to 24 hours after exposure, affected individuals need complete rest (preferably in semi-recumbent posture) and must be kept under medical observation even if no symptoms are (yet) manifested. Before any such manifestation, the administration of a spray containing a dexamethasone derivative or beclomethasone derivative may be considered. This

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must definitely be left to a doctor or person authorized by him/her. (ICSC13719).

NOTES TO PHYSICIAN

- For acute or short term repeated exposures to strong acids:
 - Airway problems may arise from laryngeal edema and inhalation exposure. Treat with 100% oxygen initially.
 - Respiratory distress may require cricothyroidotomy if endotracheal intubation is contraindicated by excessive swelling
 - Intravenous lines should be established immediately in all cases where there is evidence of circulatory compromise.
 - Strong acids produce a coagulation necrosis characterized by formation of a coagulum (eschar) as a result of the desiccating action of the acid on proteins in specific tissues.

INGESTION:

- Immediate dilution (milk or water) within 30 minutes post ingestion is recommended.
- DO NOT attempt to neutralize the acid since exothermic reaction may extend the corrosive injury.
- Be careful to avoid further vomit since re-exposure of the mucosa to the acid is harmful. Limit fluids to one or two glasses in an adult.
- Charcoal has no place in acid management.
- Some authors suggest the use of lavage within 1 hour of ingestion.

SKIN:

- Skin lesions require copious saline irrigation. Treat chemical burns as thermal burns with non-adherent gauze and wrapping.
- Deep second-degree burns may benefit from topical silver sulfadiazine.

EYE:

- Eye injuries require retraction of the eyelids to ensure thorough irrigation of the conjunctival cul-de-sacs. Irrigation should last at least 20-30 minutes. DO NOT use neutralizing agents or any other additives. Several liters of saline are required.
- Cycloplegic drops, (1% cyclopentolate for short-term use or 5% homatropine for longer term use) antibiotic drops, vasoconstrictive agents or artificial tears may be indicated dependent on the severity of the injury.
- Steroid eye drops should only be administered with the approval of a consulting ophthalmologist).

[Ellenhorn and Barceloux: Medical Toxicology].

All persons handling organic phosphorus ester materials regularly should undergo regular medical examination with special stress on the central nervous systems. Whilst atropine or pyridine-2-aldoxime methiodide (PAM) are beneficial antidotes for acute phosphate ester poisonings, they are of little value in reversing acute or chronic neurological damage due to phosphites and some types of aryl phosphate.

Section 5 - FIRE FIGHTING MEASURES

Vapor Pressure (mmHg):	0.06 (25 C)
Upper Explosive Limit (%):	Not available
Specific Gravity (water=1):	1.111
Lower Explosive Limit (%):	Not available

EXTINGUISHING MEDIA

- - Foam.
 - Dry chemical powder.
 - BCF (where regulations permit).
 - Carbon dioxide.
 - Water spray or fog - Large fires only.

FIRE FIGHTING

- - Alert Emergency Responders and tell them location and nature of hazard.
 - Wear full body protective clothing with breathing apparatus.
 - Prevent, by any means available, spillage from entering drains or water course.
 - Use fire fighting procedures suitable for surrounding area.
 - DO NOT approach containers suspected to be hot.
 - Cool fire exposed containers with water spray from a protected location.
 - If safe to do so, remove containers from path of fire.
 - Equipment should be thoroughly decontaminated after use.

GENERAL FIRE HAZARDS/HAZARDOUS COMBUSTIBLE PRODUCTS

- - Combustible.

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- Slight fire hazard when exposed to heat or flame.
- Acids may react with metals to produce hydrogen, a highly flammable and explosive gas.
- Heating may cause expansion or decomposition leading to violent rupture of rigid containers.
- May emit acrid smoke and corrosive fumes.

Combustion products include: carbon monoxide (CO), carbon dioxide (CO₂), phosphorus oxides (PO_x), sulfur oxides (SO_x), other pyrolysis products typical of burning organic material.

FIRE INCOMPATIBILITY

- Avoid contamination with oxidizing agents i.e. nitrates, oxidizing acids, chlorine bleaches, pool chlorine etc. as ignition may result.

PERSONAL PROTECTION

Glasses:

Chemical goggles.

Full face- shield.

Gloves:

Respirator:

Type AB-P Filter of sufficient capacity

Section 6 - ACCIDENTAL RELEASE MEASURES

MINOR SPILLS

-
- Drains for storage or use areas should have retention basins for pH adjustments and dilution of spills before discharge or disposal of material.
- Check regularly for spills and leaks.
- Clean up all spills immediately.
- Avoid breathing vapors and contact with skin and eyes.
- Control personal contact by using protective equipment.
- Contain and absorb spill with sand, earth, inert material or vermiculite.
- Wipe up.
- Place in a suitable labeled container for waste disposal.

MAJOR SPILLS

- Chemical Class: acidic compounds, organic

For release onto land: recommended sorbents listed in order of priority.

SORBENT TYPE	RANK	APPLICATION	COLLECTION	LIMITATIONS
LAND SPILL - SMALL				
wood fiber - pillow	1	throw	pitchfork	R, P, DGC, RT
cross-linked polymer - particulate	1	shovel	shovel	R,W,SS
cross-linked polymer - pillow	1	throw	pitchfork	R, DGC, RT
sorbent clay - particulate	2	shovel	shovel	R, I, P
foamed glass - pillow	2	throw	pitchfork	R, P, DGC, RT
wood fiber - particulate	3	shovel	shovel	R, W, P, DGC
LAND SPILL - MEDIUM				
cross-linked polymer -particulate	1	blower	skidloader	R, W, SS
polypropylene - particulate	2	blower	skidloader	W, SS, DGC
sorbent clay - particulate	2	blower	skidloader	R, I, P
cross-linked polymer - pillow	3	throw	skidloader	R, DGC, RT
polypropylene - mat	3	throw	skidloader	W, SS, DGC
expanded mineral - particulate	3	blower	skidloader	R, I, W, P, DGC

Legend

DGC: Not effective where ground cover is dense

R: Not reusable

I: Not incinerable

P: Effectiveness reduced when rainy

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RT: Not effective where terrain is rugged

SS: Not for use within environmentally sensitive sites

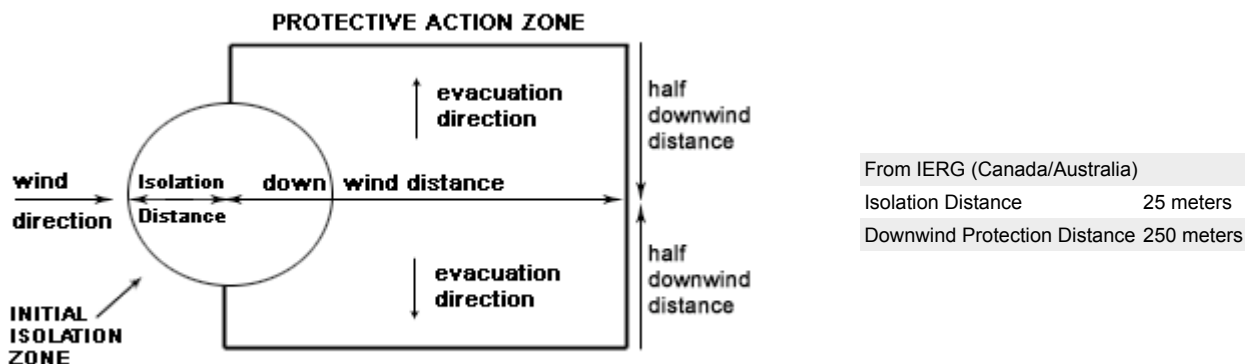
W: Effectiveness reduced when windy

Reference: Sorbents for Liquid Hazardous Substance Cleanup and Control;

R.W Melvold et al: Pollution Technology Review No. 150: Noyes Data Corporation 1988.

- Clear area of personnel and move upwind.
- Alert Emergency Responders and tell them location and nature of hazard.
- Wear full body protective clothing with breathing apparatus.
- Prevent, by any means available, spillage from entering drains or water course.
- Consider evacuation.
- Stop leak if safe to do so.
- Contain spill with sand, earth or vermiculite.
- Collect recoverable product into labeled containers for recycling.
- Neutralize/decontaminate residue.
- Collect solid residues and seal in labeled drums for disposal.
- Wash area and prevent runoff into drains.
- After clean up operations, decontaminate and launder all protective clothing and equipment before storing and re-using.
- If contamination of drains or waterways occurs, advise emergency services.

PROTECTIVE ACTIONS FOR SPILL



FOOTNOTES

1 PROTECTIVE ACTION ZONE is defined as the area in which people are at risk of harmful exposure. This zone assumes that random changes in wind direction confines the vapour plume to an area within 30 degrees on either side of the predominant wind direction, resulting in a crosswind protective action distance equal to the downwind protective action distance.

2 PROTECTIVE ACTIONS should be initiated to the extent possible, beginning with those closest to the spill and working away from the site in the downwind direction. Within the protective action zone a level of vapour concentration may exist resulting in nearly all unprotected persons becoming incapacitated and unable to take protective action and/or incurring serious or irreversible health effects.

3 INITIAL ISOLATION ZONE is determined as an area, including upwind of the incident, within which a high probability of localised wind reversal may expose nearly all persons without appropriate protection to life-threatening concentrations of the material.

4 SMALL SPILLS involve a leaking package of 200 litres (55 US gallons) or less, such as a drum (jerrican or box with inner containers). Larger packages leaking less than 200 litres and compressed gas leaking from a small cylinder are also considered "small spills". LARGE SPILLS involve many small leaking packages or a leaking package of greater than 200 litres, such as a cargo tank, portable tank or a "one-tonne" compressed gas cylinder.

5 Guide 154 is taken from the US DOT emergency response guide book.

6 IERG information is derived from CANUTEC - Transport Canada.

ACUTE EXPOSURE GUIDELINE LEVELS (AEGL) (in ppm)

AEGL 1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL 2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects

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or an impaired ability to escape.

AEGL 3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

EMERGENCY RESPONSE PLANNING GUIDELINES (ERPG)

The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour WITHOUT experiencing or developing

life-threatening health effects is:

hydrogen sulfide	100ppm
------------------	--------

irreversible or other serious effects or symptoms which could impair an individual's ability to take protective action is:

hydrogen sulfide	30ppm
------------------	-------

other than mild, transient adverse effects without perceiving a clearly defined odour is:

hydrogen sulfide	0.1ppm
------------------	--------

American Industrial Hygiene Association (AIHA)

Ingredients considered according exceed the following cutoffs

Very Toxic (T+)	>= 0.1%	Toxic (T)	>= 3.0%
R50	>= 0.25%	Corrosive (C)	>= 5.0%
R51	>= 2.5%		
else	>= 10%		

where percentage is percentage of ingredient found in the mixture

Section 7 - HANDLING AND STORAGE

PROCEDURE FOR HANDLING

-
- DO NOT allow clothing wet with material to stay in contact with skin
- Avoid all personal contact, including inhalation.
- Wear protective clothing when risk of exposure occurs.
- Use in a well-ventilated area.
- WARNING: To avoid violent reaction, ALWAYS add material to water and NEVER water to material.
- Avoid smoking, naked lights or ignition sources.
- Avoid contact with incompatible materials.
- When handling, DO NOT eat, drink or smoke.
- Keep containers securely sealed when not in use.
- Avoid physical damage to containers.
- Always wash hands with soap and water after handling.
- Work clothes should be laundered separately.
- Launder contaminated clothing before re-use.
- Use good occupational work practice.
- Observe manufacturer's storing and handling recommendations.
- Atmosphere should be regularly checked against established exposure standards to ensure safe working conditions are maintained.

RECOMMENDED STORAGE METHODS

■ DO NOT use aluminum or galvanized containers.

Check regularly for spills and leaks.

Glass container.

- Lined metal can, Lined metal pail/drum
- Plastic pail
- Polyliner drum
- Packing as recommended by manufacturer.
- Check all containers are clearly labeled and free from leaks.

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For low viscosity materials

- Drums and jerricans must be of the non-removable head type.
- Where a can is to be used as an inner package, the can must have a screwed enclosure.

For materials with a viscosity of at least 2680 cSt. (23 deg. C) and solids (between 15 C deg. and 40 deg C.):

- Removable head packaging;
- Cans with friction closures and
- low pressure tubes and cartridges may be used.

- Where combination packages are used, and the inner packages are of glass, porcelain or stoneware, there must be sufficient inert cushioning material in contact with inner and outer packages unless the outer packaging is a close fitting molded plastic box and the substances are not incompatible with the plastic.

STORAGE REQUIREMENTS

- Store in original containers.
- Keep containers securely sealed.
- Store in a cool, dry, well-ventilated area.
- Store away from incompatible materials and foodstuff containers.
- Protect containers against physical damage and check regularly for leaks.
- Observe manufacturer's storing and handling recommendations.

SAFE STORAGE WITH OTHER CLASSIFIED CHEMICALS



X: Must not be stored together

O: May be stored together with specific preventions

+: May be stored together

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m ³	STEL ppm	STEL mg/m ³	Peak ppm	Peak mg/m ³	TWA F/CC	Notes
US - Minnesota Permissible Exposure Limits (PELs)	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21				
Canada - Ontario Occupational Exposure Limits	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21				
US ATSDR Minimal Risk Levels for Hazardous Substances (MRLs)	hydrogen sulfide (HYDROGEN SULFIDE)	0.02							
US ATSDR Minimal Risk Levels for Hazardous Substances (MRLs)	hydrogen sulfide (HYDROGEN SULFIDE)	0.07							
US NIOSH Recommended Exposure Limits (RELs)	hydrogen sulfide (Hydrogen sulfide)					10	15		
Canada - British Columbia Occupational Exposure Limits	hydrogen sulfide (Hydrogen sulfide)					10			
Canada - Alberta Occupational Exposure Limits	hydrogen sulfide (Hydrogen sulphide)	10	14			15	21		

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US - Tennessee Occupational Exposure Limits - Limits For Air Contaminants	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21		
US - Idaho - Acceptable Maximum Peak Concentrations	hydrogen sulfide (Hydrogen sulfide (Z37.2-1966))				20		
US - Vermont Permissible Exposure Limits Table Z-1-A Final Rule Limits for Air Contaminants	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21	20	
US - Vermont Permissible Exposure Limits Table Z-1-A Transitional Limits for Air Contaminants	hydrogen sulfide (Hydrogen sulfide)			See Table Z-2			
US - Idaho - Limits for Air Contaminants	hydrogen sulfide (Hydrogen sulfid)		[2]				
US - California Permissible Exposure Limits for Chemical Contaminants	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21	50	
US ACGIH Threshold Limit Values (TLV)	hydrogen sulfide (Hydrogen sulfide)	10		15			
US - Michigan Exposure Limits for Air Contaminants	hydrogen sulfide (Hydrogen sulphide)	10	14	15	21		
US - Alaska Limits for Air Contaminants	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21		
Canada - Northwest Territories Occupational Exposure Limits (English)	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21	20	28
US - Washington Permissible exposure limits of air contaminants	hydrogen sulfide (Hydrogen sulfide)	10		15			
Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances	hydrogen sulfide (Hydrogen sulphide)	10	15	15	27		
US - Hawaii Air Contaminant Limits	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21		
Canada - Saskatchewan Occupational Health and Safety Regulations - Contamination Limits	hydrogen sulfide (Hydrogen sulphide)	10		15			
Canada - Quebec Permissible Exposure Values for Airborne Contaminants (English)	hydrogen sulfide (Hydrogen sulfide)	10	14	15	21		
US - Wyoming Toxic and Hazardous Substances Table Z-2 Acceptable ceiling concentration, Acceptable maximum peak above the acceptable ceiling concentration for an 8-hr shift	hydrogen sulfide (Hydrogen sulfide (Z37.2-1966))					20	
US OSHA Permissible Exposure Levels (PELs) - Table Z2	hydrogen sulfide (Hydrogen sulfide (Z37.2-1966))					20	
Canada - Nova Scotia Occupational Exposure Limits	hydrogen sulfide (Hydrogen sulfide)	10		15			
US - Oregon Permissible Exposure Limits (Z2)	hydrogen sulfide (Hydrogen sulfide (Z37.2-1966))					20	
Canada - Prince Edward Island Occupational Exposure Limits	hydrogen sulfide (Hydrogen sulfide)	10		15			

The following materials had no OELs on our records

- diethyl dithiophosphate: CAS:298-06-6

EMERGENCY EXPOSURE LIMITS

Material	Revised IDLH Value (mg/m3)	Revised IDLH Value (ppm)
hydrogen sulfide		100

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MATERIAL DATA

DIETHYL DITHIOPHOSPHATE:

HYDROGEN SULFIDE:

■ Odour Threshold Value for hydrogen sulfide: 0.0011 ppm (detection), 0.0045 ppm (recognition)

NOTE: Detector tubes for hydrogen sulfide, measuring in excess of 0.5 ppm are available commercially.

The TLV-TWA is protective against sudden death, eye irritation, neurasthenic symptoms such as fatigue, headache, dizziness, and irritability, or permanent central nervous system effects that may result from acute, subchronic, or acute exposure to hydrogen sulfide. The offensive odour of hydrogen sulfide does not give a reliable warning signal because olfactory fatigue occurs at concentrations of 150 to 200 ppm.

Hydrogen sulfide is probably the leading cause of sudden death in the workplace. Lethal hydrogen sulfide toxicity following inhalation of 1000-2000 ppm paralyses the respiratory centre and causes breathing to stop. At concentrations between 500 to 1000 ppm, the carotid bodies are stimulated causing hypernea which is followed by apnea. Low concentrations

(50-1500 ppm) produce eye and respiratory tract irritation. Prolonged exposure to concentrations of the order of 250-500 ppm may produce pulmonary oedema although 50 ppm has also reportedly produced this effect.

Concentrations in excess of 50 ppm produce acute conjunctivitis with pain, lachrymation and photophobia. These acute changes may progress to keratoconjunctivitis and vesiculation of the corneal epithelium.

Concentrations between 5 and 30 ppm produce ocular toxicity.

Odour Safety Factor(OSF)

OSF=1.2E3 (HYDROGEN SULFIDE).

HYDROGEN SULFIDE:

■ Exposed individuals are reasonably expected to be warned, by smell, that the Exposure Standard is being exceeded.

Odor Safety Factor (OSF) is determined to fall into either Class A or B.

The Odor Safety Factor (OSF) is defined as:

OSF= Exposure Standard (TWA) ppm/ Odor Threshold Value (OTV) ppm

Classification into classes follows:

Class	OSF	Description
A	550	Over 90% of exposed individuals are aware by smell that the Exposure Standard (TLV-TWA for example) is being reached, even when distracted by working activities
B	26-550	Idem for 50-90% of persons being distracted
C	1-26	Idem for less than 50% of persons being distracted
D	0.18-1	0-50% of persons aware of being tested perceive by smell that the Exposure Standard is being reached
E	<0.18	Idem for less than 10% of persons aware of being tested

Amoore and Hautala * have determined that it is only at an OSF value of 26 that 50% of distracted persons can detect the substance at the Exposure Standard value. In the case of alerted persons, an OSF of 26 means that 99% of them can detect the odor at the Exposure Standard value. It is ONLY for substances belonging to Class A and B that there is a reasonable chance of being warned in time, that the Exposure Standard is being exceeded. * Journal Applied Toxicology: Vol 3, 1983, p272

NOTE: The use of the OSF may be inappropriate for mixtures where substances mask the odor of others.

PERSONAL PROTECTION



Consult your EHS staff for recommendations

EYE

-
- Chemical goggles.
- Full face shield.

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Hazard Alert Code Key:	EXTREME	HIGH	MODERATE	LOW
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- Contact lenses pose a special hazard; soft contact lenses may absorb irritants and all lenses concentrate them.

HANDS/FEET

- Elbow length PVC gloves.

- When handling corrosive liquids, wear trousers or overalls outside of boots, to avoid spills entering boots.

Suitability and durability of glove type is dependent on usage. Important factors in the selection of gloves include: such as:

- frequency and duration of contact,
- chemical resistance of glove material,
- glove thickness and
- dexterity

Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739).

- When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374) is recommended.
- When only brief contact is expected, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN 374) is recommended.
- Contaminated gloves should be replaced.

Gloves must only be worn on clean hands. After using gloves, hands should be washed and dried thoroughly. Application of a non-perfumed moisturiser is recommended.

OTHER

-
- Overalls.
- PVC Apron.
- PVC protective suit may be required if exposure severe.
- Eyewash unit.
- Ensure there is ready access to a safety shower.

RESPIRATOR

- Selection of the Class and Type of respirator will depend upon the level of breathing zone contaminant and the chemical nature of the contaminant. Protection Factors (defined as the ratio of contaminant outside and inside the mask) may also be important.

Breathing Zone Level ppm (volume)	Maximum Protection Factor	Half-face Respirator	Full-Face Respirator
1000	10	AB-1 P	-
1000	50	-	AB-1 P
5000	50	Airline*	-
5000	100	-	AB-2 P
10000	100	-	AB-3 P
	100+		Airline* *

* - Continuous Flow ** - Continuous-flow or positive pressure demand.

The local concentration of material, quantity and conditions of use determine the type of personal protective equipment required.

Use appropriate NIOSH-certified respirator based on informed professional judgement. In conditions where no reasonable estimate of exposure can be made, assume the exposure is in a concentration IDLH and use NIOSH-certified full face pressure demand SCBA with a minimum service life of 30 minutes, or a combination full facepiece pressure demand SAR with auxiliary self-contained air supply. Respirators provided only for escape from IDLH atmospheres shall be NIOSH-certified for escape from the atmosphere in which they will be used.

ENGINEERING CONTROLS

- Local exhaust ventilation usually required. If risk of overexposure exists, wear an approved respirator. Correct fit is essential to obtain adequate protection an approved self contained breathing apparatus (SCBA) may be required in some situations. Provide adequate ventilation in warehouse or closed storage area.

Air contaminants generated in the workplace possess varying "escape" velocities which, in turn, determine the "capture velocities" of fresh circulating air required to effectively remove the contaminant.

Type of Contaminant:	Air Speed:
solvent, vapors, degreasing etc., evaporating from tank (in still air).	0.25-0.5 m/s (50-100 f/min.)
aerosols, fumes from pouring operations, intermittent container filling, low speed conveyer transfers, welding, spray drift, plating acid fumes, pickling (released at low velocity into zone of active generation)	0.5-1 m/s (100-200 f/min.)
direct spray, spray painting in shallow booths, drum filling, conveyer loading, crusher dusts, gas discharge (active generation into zone of rapid air motion)	1-2.5 m/s (200-500 f/min.)

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grinding, abrasive blasting, tumbling, high speed wheel generated dusts (released at high initial velocity into zone of very high rapid air motion). 2.5-10 m/s (500-2000 f/min.)

Within each range the appropriate value depends on:

Lower end of the range	Upper end of the range
1: Room air currents minimal or favorable to capture	1: Disturbing room air currents
2: Contaminants of low toxicity or of nuisance value only.	2: Contaminants of high toxicity
3: Intermittent, low production.	3: High production, heavy use
4: Large hood or large air mass in motion	4: Small hood-local control only

Simple theory shows that air velocity falls rapidly with distance away from the opening of a simple extraction pipe. Velocity generally decreases with the square of distance from the extraction point (in simple cases). Therefore the air speed at the extraction point should be adjusted, accordingly, after reference to distance from the contaminating source. The air velocity at the extraction fan, for example, should be a minimum of 1-2 m/s (200-400 f/min) for extraction of solvents generated in a tank 2 meters distant from the extraction point. Other mechanical considerations, producing performance deficits within the extraction apparatus, make it essential that theoretical air velocities are multiplied by factors of 10 or more when extraction systems are installed or used.

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Corrosive.

Acid.

Toxic or noxious vapors/ gas.

State	LIQUID	Molecular Weight	186.23
Melting Range (°F)	Not available	Viscosity	Not Available
Boiling Range (°F)	140 (1 mm Hg)	Solubility in water (g/L)	Reacts
Flash Point (°F)	179.6	pH (1% solution)	Not available
Decomposition Temp (°F)	Not Available	pH (as supplied)	Not available
Autoignition Temp (°F)	Not available	Vapor Pressure (mmHg)	0.06 (25 C)
Upper Explosive Limit (%)	Not available	Specific Gravity (water=1)	1.111
Lower Explosive Limit (%)	Not available	Relative Vapor Density (air=1)	Not available.
Volatile Component (%vol)	Negligible	Evaporation Rate	Very Slow

APPEARANCE

Blue green liquid which hydrolyses in water. The properties of DEA (a common abbreviation for diethyl dithiophosphate) can be found in various online databases and some endpoints were calculated with EPIWin Modeling Program. DEA is a liquid at ambient temperatures and decomposes before boiling. The calculated octanol/water partition coefficient is 1.17 and only the salt form is soluble in water

Section 10 - CHEMICAL STABILITY

CONDITIONS CONTRIBUTING TO INSTABILITY

-
- Contact with alkaline material liberates heat
- Presence of incompatible materials.
- Product is considered stable.
- Hazardous polymerization will not occur.

STORAGE INCOMPATIBILITY

- Hydrogen sulfide (H₂S):
- is a highly flammable and reactive gas
- reacts violently with strong oxidisers, metal oxides, metal dusts and powders, bromine pentafluoride, chlorine trifluoride, chromium trioxide, chromyl chloride, dichlorine oxide, nitrogen trichloride, nitril hypofluorite, oxygen difluoride, perchloryl fluoride, phospham,

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- phosphorus persulfide, silver fulminate, soda-lime, sodium peroxide
- is incompatible with acetaldehyde, chlorine monoxide, chromic acid, chromic anhydride, copper, nitric acid, phenyldiazonium chloride, sodium
 - forms explosive material with benzenediazonium salts
 - attacks many metals

Flow or agitation of hydrogen sulfide may generate electrostatic charges due to low conductivity.

A number of phosphate and thiophosphate esters are of limited thermal stability and undergo highly exothermic self-accelerating decomposition reactions which may be catalyzed by impurities. The potential hazards can be reduced by appropriate thermal control measures.

BREThERICK L.: Handbook of Reactive Chemical Hazards.

Reacts with mild steel, galvanized steel / zinc producing hydrogen gas which may form an explosive mixture with air.

Avoid storage with reducing agents.

- Sulfides are incompatible with acids, diazo and azo compounds, halocarbons, isocyanates, aldehydes, alkali metals, nitrides, hydrides, and other strong reducing agents.
- Many reactions of sulfides with these materials generate heat and in many cases hydrogen gas.
- Many sulfide compounds may liberate hydrogen sulfide upon reaction with an acid.

Segregate from alcohol, water.

Segregate from alkalis, oxidizing agents and chemicals readily decomposed by acids, i.e. cyanides, sulfides, carbonates.

- Avoid strong acids, bases.
- Alkyl esters of thiophosphates are often temperature sensitive and decompose if overheated. Thermal decomposition products include highly toxic and odiferous hydrogen sulfide and extremely odorous alkyl mercaptans. Both species can be detected at extremely low concentrations and vapors may travel long distances.
- Low temperature storage may produce crystallization from solution.
- CARE: If heating to liquefy, use tepid water, Avoid temperatures in excess of 50 deg. C.
- Head-space of drums may contain hydrogen sulfide.
- NOTE: May develop pressure in containers; open carefully. Vent periodically.

For incompatible materials - refer to Section 7 - Handling and Storage.

Section 11 - TOXICOLOGICAL INFORMATION

diethyl dithiophosphate

TOXICITY AND IRRITATION

■ unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY	IRRITATION
Oral (rat) LD50: 4510 mg/kg	Skin (rabbit): 500 mg/24h - Mild
Inhalation (Rat) LC50: 1640 mg/m ³ /4h	Eye (rabbit): 0.05 mg/24h-SEVERE

Dermal (Rabbit) LD50: >2000 mg/kg *

■ Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a non-allergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound. Key criteria for the diagnosis of RADS include the absence of preceding respiratory disease, in a non-atopic individual, with abrupt onset of persistent asthma-like symptoms within minutes to hours of a documented exposure to the irritant. A reversible airflow pattern, on spirometry, with the presence of moderate to severe bronchial hyperreactivity on methacholine challenge testing and the lack of minimal lymphocytic inflammation, without eosinophilia, have also been included in the criteria for diagnosis of RADS. RADS (or asthma) following an irritating inhalation is an infrequent disorder with rates related to the concentration of and duration of exposure to the irritating substance. Industrial bronchitis, on the other hand, is a disorder that occurs as result of exposure due to high concentrations of irritating substance (often particulate in nature) and is completely reversible after exposure ceases. The disorder is characterised by dyspnea, cough and mucus production.

The material may produce severe irritation to the eye causing pronounced inflammation. Repeated or prolonged exposure to irritants may produce conjunctivitis.

The material may produce respiratory tract irritation, and result in damage to the lung including reduced lung function.

The material may cause skin irritation after prolonged or repeated exposure and may produce on contact skin redness, swelling, the production of vesicles, scaling and thickening of the skin.

For dithiophosphate alkyl esters and their (zinc) salts:

Acute toxicity: Dithiophosphate alkyl esters consist of a phosphorodithioic acid structure with alkyl ester substituent groups. The alkyl groups are saturated hydrocarbon chains that vary in length and extent of branching. While corrosive to tissue the esters demonstrate a low concern for acute systemic toxicity. Data on acute mammalian toxicity of zinc dialkyldithiophosphates in highly refined lubricant base oil also indicate a

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low concern for acute toxicity. Commercial oil-based samples of the zinc dialkyldithiophosphate category have been tested for acute oral toxicity. The acute oral LD50 for these studies in rats ranged from 2000-3500 mg/kg. Clinical signs observed following treatment included diarrhea, lethargy, reduced food consumption, and staining about the nose and eye. Ptosis, piloerection, ataxia and salivation were occasionally observed. The incidence and severity of these symptoms were proportional to the dose. In many cases the effects were found to be reversible during observation week 2. Necropsy findings were few in number. Lung congestion, gastrointestinal irritation and a reduction in body fat were observed in some animals.

Acute dermal toxicity and irritation studies using the ester on experimental animals resulted in severe dermal irritation and corrosivity. There is minimal opportunity of human exposure to the chemicals in this category. Dithiophosphate alkyl esters exhibit extreme corrosive properties on skin.

Commercial oil-based samples of the zinc dialkyldithiophosphate category have been tested for acute dermal toxicity. The acute dermal LD50s for these studies in rabbits were greater than 2000 mg/kg (limit tests). No treatment-related mortality was observed at doses ranging from 2000-8000 mg/kg. Dermal application of the test materials to abraded skin for 24 hours typically produced moderate-to-severe erythema and edema, which in some cases persisted through the 14-day observation period. Clinical signs included varying degrees of reduced food consumption, weight loss, diarrhea, lethargy, ataxia, ptosis, motor incoordination and/or loss of righting reflex. There were no remarkable gross necropsy observations. Overall, the acute dermal LD50 for these substances were greater than 2000 mg/kg indicative of a relatively low order of lethal toxicity. Zinc dialkyldithiophosphates are high molecular weight components (average > 500 gm/mol), which generally accepted that the molecular weight limit for passive transport across biological membranes. Thus, upon exposure it is unlikely that significant amounts of these components will be absorbed for systemic distribution. In addition, these materials have a low water solubility that further inhibits absorption and distribution in the mammalian system.

The negligible vapor pressure and high viscosity at ambient temperature indicates that these materials are unlikely to represent an inhalation exposure under conditions of use

Repeat dose toxicity: Data from several repeated-dose toxicity studies using commercial samples of zinc dialkyldithiophosphates in highly refined lubricant base oil has been reviewed. Repeated dermal exposure to experimental animals resulted in moderate-to-severe dermal irritation, behavioral distress, body weight loss and emaciation, reduction in hematological parameters and adverse effects on male reproductive organs. These effects were observed across several members of the category with carbon chain lengths ranging from C4-8. There was no evidence that the incremental increase in carbon chain length or molecular weight could be correlated with significant changes in toxicity parameters.

Oral administration caused significant gastric irritation and related gastrointestinal disturbances, signs of distress but with no evidence of adverse effects on male reproductive organs.

Reproductive toxicity: An epidemiological study on workers exposed to oil-based zinc dialkyldithiophosphates (range C4-8) in an additive manufacturing plant revealed no adverse effects on worker reproductive health. Review of the available information underscores the similarity of clinical and pathological findings in repeated-dose dermal toxicity studies with C4-10 zinc dialkyldithiophosphates, as well as the absence of reproduction and developmental toxicity and the lack of untoward findings in a human epidemiological investigation. Reproductive organ effects, following dermal application, have been observed in male rabbits; these are attributed to the stress associated with the severe dermal responses to the test material, rather than direct a systemic response to the test materials. Changes in male reproductive organs in the rabbit have been observed when other irritating substances are applied to the skin at dose levels that cause skin lesions. Thus, dermal irritation alone, or in combination with the accompanying weight loss and stress, is thought to play a role in the reproductive organ response to repeated cutaneous application of zinc dialkyldithiophosphates.

Mutagenicity: Findings indicate that commercial samples of zinc dialkyldithiophosphates in highly refined lubricant base oil have a small potential for inducing genetic toxicity. In vitro bacterial gene mutation assays, in vitro mammalian gene mutation assays, or in vivo chromosomal aberration assays have been conducted. Frequencies of reverse mutations in bacteria were not significantly changed after exposure to the zinc dialkyldithiophosphates. In vitro mutation studies in mammalian cells indicate that the zinc dialkyldithiophosphates do not consistently display mutagenic activity in the absence of metabolic activation, however, upon biotransformation, these materials showed mutagenic activity. The findings in bacterial and mammalian cells did not vary in proportion to the alkyl chain length or any other physicochemical parameter.

The results of the studies performed in the absence of hepatic microsome activation were inconsistent, but in general indicating that zinc dialkyldithiophosphates have mutagenic potential (3 studies negative, 3 studies positive in the absence of metabolic activation). However, the weight of evidence (2 studies positive, 1 study negative) indicates that metabolic activation of zinc dialkyldithiophosphates by induced hepatic microsomal enzymes results in a significant increase in the mutagenic potential of this class of chemical substances.

Low concern for acute mammalian toxicity [Bayer]

Toxicity studies in animals show that DEA (the substance) is of low acute toxicity by all routes of exposure

There is an Ames study on DEA suggesting mutagenicity. No studies on chromosome aberration were located.

There were no repeat dose, fertility, nor developmental studies found.

DEA is irritating to the skin and eyes of rabbits.

*Bayer

HYDROGEN SULFIDE:

■ unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY	IRRITATION
Inhalation (human) LDLo: 5.7 mg/kg	Nil Reported

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Inhalation (human) LCLo: 600 ppm/30m

Inhalation (human) LCLo: 800 ppm/5m

Section 12 - ECOLOGICAL INFORMATION

Refer to data for ingredients, which follows:

HYDROGEN SULFIDE:

DIETHYL DITHIOPHOSPHATE:

- DO NOT discharge into sewer or waterways.

- For hydrogen sulfide:

Environmental fate:

Since hydrogen sulfide exists as a gas at atmospheric pressure, partitioning to the air is likely to occur after environmental releases. However, the compound is also soluble in oil and water, and therefore, may partition as well to surface water, groundwater, or moist soil. In addition, sorption of hydrogen sulfide from air onto soil and plant foliage occurs. Hydrogen sulfide's solubility in pure water varies with temperature from 5.3 g/L at 10 °C to 3.2 g/L at 30 C. Once hydrogen sulfide is dissolved in water, it will dissociate into bisulfide ion (HS⁻) and sulfide ion (S²⁻); the ratio of the concentrations of these various ions will depend on the pH of the solution. Hydrogen sulfide can also form insoluble sulfide salts with various metals (i.e., copper, zinc, nickel, and iron) that may be present in soils or environmental waters .

Hydrogen sulfide evaporates easily from water, and the rate of evaporation depends on factors such as temperature, humidity, pKa, pH, and the concentration of certain metal ions. Hydrogen sulfide will cross the air-water interface with kinetics similar to other unreactive gases, such as oxygen (O₂), nitrogen (N₂), and carbon dioxide (CO₂), at pHs <=6. At higher pHs, such as seawater, which has a pH of 8 or greater, hydrogen sulfide escape is enhanced due to an ionic species gradient in the water close to the surface. Complexation of bisulfide and sulfide ions to trace metal ions (i.e., Zn²⁺, Co²⁺, and Ni²⁺) found in seawater will also have an effect on the transport of hydrogen sulfide across the air-water interface.

Clay or organic matter may sorb hydrogen sulfide. Under natural conditions, it is likely that some of the hydrogen sulfide would be oxidized to sulfate, which may be removed by leaching or taken up by plants. This, in turn, may make gas sorption sites available for additional sorption. Several species of soil, aquatic, and marine microorganisms oxidize hydrogen sulfide to elemental sulfur, and its half-time in these environments usually ranges from 1 hour to several hours .Food chain bioconcentration and biomagnification are unlikely.

In the atmosphere, hydrogen sulfide may be oxidized by oxygen (O₂) and ozone (O₃) to give sulfur dioxide (SO₂), and ultimately sulfate compounds. Sulfur dioxide and sulfates are eventually removed from the atmosphere through absorption by plants, deposition on and sorption by soils, or through precipitation. A residence time of approximately 1.7 days at an ozone concentration of 0.05 mg/m³ has been calculated for hydrogen sulfide. The effective life-times for hydrogen sulfide based on summer daytime and yearly average hydroxyl radical concentrations have been estimated to be 0.23 and 2.3 days, respectively, based a measured rate constant of 4.8x10⁻¹² cm³/molecule second. Life-times in air ranging from approximately 1 day in the summer to 42 days in the winter have been estimated for hydrogen sulfide. Hydrogen sulfide is not expected to be decomposed by direct absorption of ultraviolet radiation and the reaction with ozone is not expected to be a significant environmental fate.

In aqueous solution, hydrogen sulfide is a weak acid, exhibiting two acid dissociation constants. The first dissociation yields bisulfide ion (HS⁻), and the second yields sulfide ion (S²⁻), with pKa values for each of these dissociations of 7.04 and 11.96, respectively. At a pH of 7.0, the ratio of the concentration of aqueous hydrogen sulfide to bisulfate ion is approximately 1-to-1. As the pH increases above 7.0, the ratio of the concentration of bisulfide ion to aqueous hydrogen sulfide increases. At a pH of 8, the ratio of the concentration of bisulfide ion to the concentration of aqueous hydrogen sulfide is approximately 10-to-1. The relative concentration of sulfide ion does not begin to increase until a pH of 11 is exceeded; only above pH 12 will the concentration of sulfide ion become significant (>50%). Hydrogen sulfide oxidation by O₂ readily occurs in surface waters. At 25 °C and pH 8, half-times of 50 and 26 hours were reported for hydrogen sulfide in water and seawater, respectively. Above pH 8, however, the rate of oxidation was independent of pH.

Hydrogen sulfide in waste water may be controlled by addition of oxidizing chemicals, which react to form less toxic byproducts. In warm, damp environments (such as manholes and gravity sewers), hydrogen sulfide may be oxidized by autotrophic bacteria to sulfuric acid . Chemical oxidation of hydrogen sulfide dissolved in sewage water produces sulfur at pH 6–7, while sulfur, polysulfides, thiosulfates, and ultimately sulfate are formed at pHs of 7–9.

Hydrogen sulfide is one of the principal components in the natural sulfur cycle. Bacteria, fungi, and actinomycetes (a fungus-like bacteria) release hydrogen sulfide during the decomposition of sulfur containing proteins and by the direct reduction of sulfate (SO₄²⁻). Hydrogen sulfide is also consumed by bacteria found in soil and water that oxidize hydrogen sulfide to elemental sulfur. Photosynthetic bacteria can oxidize hydrogen sulfide to sulfur and sulfate in the presence of light and the absence of oxygen.

A number of microorganisms have been found to degrade hydrogen sulfide to elemental sulfur or sulfate. Among these are a heterotrophic bacterium of the genus Xanthomonas isolated from dimethyl disulfide-acclimated peat, heterotrophic fungi, and a marine isopod. Soils may sorb considerable amounts of hydrogen sulfide from the air, retaining most of it in the form of elemental sulfur. Manganese compound found in these soils appeared to catalyze the oxidation of hydrogen sulfide to elemental sulfur

Ecotoxicity:

Fish LC50 (96 h): 075->0.4 mg/l.

- Sulfide ion is very toxic to aquatic life, threshold concentration for fresh or saltwater fish is 0.5ppm. The product therefore is very toxic to

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aquatic life. The major decomposition product, hydrogen sulfide, is damaging to vegetation at 5ppm for 24 hours.

■ Do NOT allow product to come in contact with surface waters or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment wash-waters.

Wastes resulting from use of the product must be disposed of on site or at approved waste sites.

■ Very toxic to aquatic organisms.

DIETHYL DITHIOPHOSPHATE:

■ Ecotoxicity:

The tolerance of water organisms towards pH margin and variation is diverse. Recommended pH values for test species listed in OECD guidelines are between 6.0 and almost 9. Acute testing with fish showed 96h-LC50 at about pH 3.5.

■ For dithiophosphate alkyl esters and their (zinc) salts:

The physicochemical properties of dithiophosphate alkyl esters parallel their structural similarity. All members of this category are within a narrow molecular weight range (256-354 daltons) and are highly acidic. In addition, modeling data indicate they have similar melting and boiling points, low water solubility, low vapor pressure, and are lipophilic in nature.

Modeling data indicates that the vapor pressure of these substances range from 3.46×10^{-3} to 1.9×10^{-5} mm Hg at 25 C and generally follow a pattern based upon their molecular weight and the extent of branching of the alkyl side chain.

Modeling data indicates that these substances have low water solubility and that the log of the octanol-water partition coefficient (log Kow) of these substances range from 4.48-7.99. The low water solubility is consistent with the high lipophilic nature of these substances.

Members of the zinc dialkyldithiophosphate category, described here, contain alkyl chain lengths that range from C3-10, or tetrapropenylphenol (range = C10-15, C12 enriched). It is common for zinc dialkyldithiophosphates to contain mixed alkyl esters (e.g., C4, C5), although derivatives with single chain lengths (e.g., C8) are included in the category. As a result of this diversity in alkyl side chain length, the molecular weight distribution for the members of the category is broad, 578 to 1303 gm/mol. Due to the predominant influence of carbon chain length on molecular weight.

Vapour pressures for the zinc dialkyldithiophosphates are thought to be less than 0.5 mm Hg.

Unpublished data for a commercial zinc dialkyldithiophosphate with an alkyl group less than C8 indicates a water solubility of 1.6 mg/L. The zinc dialkyldithiophosphates are generally regarded to be poorly soluble in water.

Unpublished company data on a commercial zinc dialkyldithiophosphate with a carbon chain length of less than eight yielded a log Kow value of 2.49. Longer chain materials are likely to have higher octanol/water partition coefficients. The log Kow is a measure of the lipophilicity of a substance and is used as a surrogate indicator of the potential of a chemical substance to bioaccumulate in aquatic organisms. While Log Kow is a good predictor of bioaccumulation for nonpolar organic compounds, the mechanisms for uptake and depuration of metals and metal compounds are very complex and variable. For metal compounds, the Log Kow data are not indicative of the bioaccumulation potential.

Fate and Transport Characteristics. Members of this category are expected to be poorly biodegradable.

The members of the category are resistant to hydrolysis at room temperature because they lack readily hydrolysable moieties. When heated hydrolytic degradation results in the formation of the phosphorothioic acid ester and hydrogen sulfide. Continued heating at high temperatures results in the formation of the mono-ester and eventually, phosphorothioic acid itself.

These materials are known to be thermally labile at temperatures >120 C. This decomposition mechanism is key to how the zinc salts provide anti-wear and anti-oxidation performance enhancements in engine oils.

Photodegradation is not expected to cause significant physical degradation of dithiophosphate alkyl esters. Category members do not contain bonds that have a high potential to absorb UV light above 290 nm. These substances have low vapor pressure, which indicates that they have a low potential to partition into the air to a significant extent where they would be subject to indirect photodegradation.

These substances are not expected to partition to water or air if released into the environment due to their low water solubility and low vapor pressure. They are also hydrophobic in nature, which suggests that any which reaches the water compartment will be immobilized through binding to the organic component of soils and sediments.

A Japanese MITI publication cited a bioaccumulation factor of less than 100 for a C4-5 ester zinc dithiophosphate indicating a low potential for bioconcentration or cumulative effects.

The hydrocarbon portion of these compounds that is susceptible to biodegradation is present in both the zinc dialkyldithiophosphates and the dithiophosphate alkyl esters. Therefore, it is expected that the dithiophosphate alkyl esters will behave similarly. The zinc salts are poorly biodegradable.

Ecotoxicity:

The low water solubility suggests that the acute aquatic toxicity of these substances should be low due to limited bioavailability to aquatic organisms. However, the length of the alkyl side chains on these substances will influence their relative water solubility, and, hence, their relative toxicity. Diethyl dithiophosphate for example is highly toxic to Daphnids

Zinc O,O-bis(isooctyl)dithiophosphate (CAS RN 28629-66-5) also appears to be harmful to aquatic organisms such as fish and Daphnids.

■ Studies on various thiophosphates indicated complete mineralization within three weeks by acclimation. A water stability study demonstrated the nature of hydrolysis involves the attack of water molecule on the phosphorus ester involving P-O bond fission.

■ Prevent, by any means available, spillage from entering drains or watercourses.

For diethyl dithiophosphate

log Kow 1.17 (calc)

Fish LC50 (96 h): Salmo gairdineri 310-330 mg/l

Daphnia magna LC50 (24 h) 0.54 mg/l

Environmental Fate:

Photodegradation was calculated as a half-life of 1.4 hours for DEA the common abbreviation for the substance). Fugacity modeling demonstrates partitioning to the soil and water compartments. Biodegradation modeling demonstrates that DEA is biodegradable. In addition,

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a well documented study on various thiophosphates indicated complete mineralization within three weeks by acclimation. A water stability study demonstrated the nature of hydrolysis involves the attack of water molecule on the phosphorus of the di-ester involving P-O bond fission. .

Ecotoxicology:

Aquatic studies have been performed on *Salmo gairdineri*, *Poecilia reticulata* and on *Daphnia magna*.

Fish LC50 (96 h): *Salmo gairdineri* 310-330 mg/l

Daphnia magna LC50 (24 h) 0.54 mg/l (highly toxic)

HYDROGEN SULFIDE:

■ Fish LC50 (96hr.) (mg/l): 0.0071- 0.5

■ The material is classified as an ecotoxin* because the Fish LC50 (96 hours) is less than or equal to 0.1 mg/l

* Classification of Substances as Ecotoxic (Dangerous to the Environment)

Appendix 8, Table 1

Compiler's Guide for the Preparation of International Chemical Safety Cards: 1993 Commission of the European Communities.

Fish LC50 (96 h): 075->0.4 mg/l

Ecotoxicity

Ingredient	Persistence: Water/Soil	Persistence: Air	Bioaccumulation	Mobility
diethyl dithiophosphate	HIGH		LOW	HIGH
hydrogen sulfide	LOW		LOW	HIGH

Section 13 - DISPOSAL CONSIDERATIONS

US EPA Waste Number & Descriptions

A. General Product Information

Corrosivity characteristic: use EPA hazardous waste number D002 (waste code C)

B. Component Waste Numbers

When hydrogen sulfide is present as a solid waste as a discarded commercial chemical product, off-specification species, as a container residue, or a spill residue, use EPA waste number U135 (waste code T).

Disposal Instructions

All waste must be handled in accordance with local, state and federal regulations.

! Puncture containers to prevent re-use and bury at an authorized landfill.

Legislation addressing waste disposal requirements may differ by country, state and/ or territory. Each user must refer to laws operating in their area. In some areas, certain wastes must be tracked.

A Hierarchy of Controls seems to be common - the user should investigate:

- Reduction,
- Reuse
- Recycling
- Disposal (if all else fails)

This material may be recycled if unused, or if it has not been contaminated so as to make it unsuitable for its intended use. If it has been contaminated, it may be possible to reclaim the product by filtration, distillation or some other means. Shelf life considerations should also be applied in making decisions of this type. Note that properties of a material may change in use, and recycling or reuse may not always be appropriate.

DO NOT allow wash water from cleaning equipment to enter drains. Collect all wash water for treatment before disposal.

- Recycle wherever possible.
- Consult manufacturer for recycling options or consult Waste Management Authority for disposal if no suitable treatment or disposal facility can be identified.
- Treat and neutralize at an approved treatment plant. Treatment should involve: Neutralization with soda-ash or soda-lime followed by: Burial in a licensed land-fill or Incineration in a licensed apparatus
- Decontaminate empty containers with 5% aqueous sodium hydroxide or soda ash, followed by water. Observe all label safeguards until containers are cleaned and destroyed.

Section 14 - TRANSPORTATION INFORMATION

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Hazard Alert Code Key: **EXTREME** **HIGH** **MODERATE** **LOW**



DOT:

Symbols:	None	Hazard class or Division:	8
Identification Numbers:	UN2922	PG:	II
Label Codes:	8, 6.1	Special provisions:	B3, IB2, T7, TP2
Packaging: Exceptions:	154	Packaging: Non-bulk:	202
Packaging: Exceptions:	154	Quantity limitations: Passenger aircraft/rail:	1 L
Quantity Limitations: Cargo aircraft only:	30 L	Vessel stowage: Location:	B
Vessel stowage: Other:	40		

Hazardous materials descriptions and proper shipping names:

Corrosive liquids, toxic, n.o.s.

Air Transport IATA:

ICAO/IATA Class:	8 (6.1)	ICAO/IATA Subrisk:	None
UN/ID Number:	2922	Packing Group:	II
Special provisions:	A3		

- Air transport may be forbidden if this material is flammable, corrosive or toxic gases may be released under normal conditions of transport.

Shipping Name: CORROSIVE LIQUID, TOXIC, N.O.S. *(CONTAINS DIETHYL DITHIOPHOSPHATE)

Maritime Transport IMDG:

IMDG Class:	8	IMDG Subrisk:	6.1
UN Number:	2922	Packing Group:	II
EMS Number:	F-A,S-B	Special provisions:	274 944

Limited Quantities: 1 L

Shipping Name: CORROSIVE LIQUID, TOXIC, N.O.S.(contains diethyl dithiophosphate)

Section 15 - REGULATORY INFORMATION

diethyl dithiophosphate (CAS: 298-06-6) is found on the following regulatory lists;

"Canada Non-Domestic Substances List (NDSL)", "OECD Representative List of High Production Volume (HPV) Chemicals", "The Australia Group Export Control List: Chemical Weapons Precursors", "US EPA High Production Volume Program Chemical List", "US Toxic Substances Control Act (TSCA) - Inventory"

Regulations for ingredients

hydrogen sulfide (CAS: 7783-06-4) is found on the following regulatory lists;

"Canada - Alberta Ambient Air Quality Objectives", "Canada - Alberta Ambient Air Quality Objectives - Other", "Canada - Alberta Occupational Exposure Limits", "Canada - British Columbia Occupational Exposure Limits", "Canada - Northwest Territories Occupational Exposure Limits (English)", "Canada - Nova Scotia Occupational Exposure Limits", "Canada - Ontario Occupational Exposure Limits", "Canada - Prince Edward Island Occupational Exposure Limits", "Canada - Quebec Permissible Exposure Values for Airborne Contaminants (English)", "Canada - Saskatchewan Occupational Health and Safety Regulations - Contamination Limits", "Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances", "Canada Ingredient Disclosure List (SOR/88-64)", "Canada National Pollutant Release Inventory (NPRI)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (English)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (French)", "International Council of Chemical

O,O'-Diethyl dithiophosphate

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Associations (ICCA) - High Production Volume List", "OECD Representative List of High Production Volume (HPV) Chemicals", "US - Alaska Limits for Air Contaminants", "US - California Air Toxics ""Hot Spots"" List (Assembly Bill 2588) Substances for which emissions must be quantified", "US - California Occupational Safety and Health Regulations (CAL/OSHA) - Hazardous Substances List", "US - California OEHHA/ARB - Acute Reference Exposure Levels and Target Organs (RELs)", "US - California OEHHA/ARB - Chronic Reference Exposure Levels and Target Organs (CRELs)", "US - California Permissible Exposure Limits for Chemical Contaminants", "US - California Toxic Air Contaminant List Category II", "US - Connecticut Hazardous Air Pollutants", "US - Hawaii Air Contaminant Limits", "US - Idaho - Acceptable Maximum Peak Concentrations", "US - Idaho - Limits for Air Contaminants", "US - Massachusetts Oil & Hazardous Material List", "US - Michigan Exposure Limits for Air Contaminants", "US - Minnesota Hazardous Substance List", "US - Minnesota Permissible Exposure Limits (PELs)", "US - New Jersey Right to Know Hazardous Substances", "US - Oregon Hazardous Materials", "US - Oregon Permissible Exposure Limits (Z1)", "US - Oregon Permissible Exposure Limits (Z2)", "US - Pennsylvania - Hazardous Substance List", "US - Rhode Island Hazardous Substance List", "US - Tennessee Occupational Exposure Limits - Limits For Air Contaminants", "US - Vermont Hazardous Constituents", "US - Vermont Hazardous wastes which are Discarded Commercial Chemical Products or Off-Specification Batches of Commercial Chemical Products or Spill Residues of Either", "US - Vermont Permissible Exposure Limits Table Z-1-A Final Rule Limits for Air Contaminants", "US - Vermont Permissible Exposure Limits Table Z-1-A Transitional Limits for Air Contaminants", "US - Washington Dangerous waste constituents list", "US - Washington Discarded Chemical Products List - ""U"" Chemical Products", "US - Washington Permissible exposure limits of air contaminants", "US - Wyoming List of Highly Hazardous Chemicals, Toxics and Reactives", "US - Wyoming Toxic and Hazardous Substances Table Z1 Limits for Air Contaminants", "US - Wyoming Toxic and Hazardous Substances Table Z-2 Acceptable ceiling concentration, Acceptable maximum peak above the acceptable ceiling concentration for an 8-hr shift", "US ACGIH Threshold Limit Values (TLV)", "US ACGIH Threshold Limit Values (TLV) - Notice of Intended Changes", "US ATSDR Minimal Risk Levels for Hazardous Substances (MRLs)", "US CERCLA Priority List of Hazardous Substances", "US CWA (Clean Water Act) - Reportable Quantities of Designated Hazardous Substances", "US Department of Homeland Security Chemical Facility Anti-Terrorism Standards - Chemicals of Interest", "US Department of Transportation (DOT) List of Hazardous Substances and Reportable Quantities - Hazardous Substances Other Than Radionuclides", "US DOE Temporary Emergency Exposure Limits (TEELs)", "US EPA Acute Exposure Guideline Levels (AEGLs) - Interim", "US EPA National Priorities List - Superfund Chemical Data Matrix (SCDM) - Hazard Ranking System - Hazardous Substance Benchmarks", "US Food Additive Database", "US List of Lists - Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-to-Know Act (EPCRA) and Section 112(r) of the Clean Air Act", "US NFPA 45 Fire Protection for Laboratories Using Chemicals - Flammability Characteristics of Common Compressed and Liquefied Gases", "US NIOSH Recommended Exposure Limits (RELs)", "US OSHA List of Highly Hazardous Chemicals, Toxics and Reactives", "US OSHA Permissible Exposure Levels (PELs) - Table Z1", "US OSHA Permissible Exposure Levels (PELs) - Table Z2", "US Postal Service (USPS) Hazardous Materials Table: Postal Service Mailability Guide", "US RCRA (Resource Conservation & Recovery Act) - Hazardous Constituents - Appendix VIII to 40 CFR 261", "US RCRA (Resource Conservation & Recovery Act) - List of Hazardous Wastes", "US SARA Section 302 Extremely Hazardous Substances", "US Toxic Substances Control Act (TSCA) - Inventory", "USA: Chemical Facility Anti-Terrorism Standards - List Appendix A - 6CFR 27", "WHO Guidelines for Drinking-water Quality - Chemicals for which guideline values have not been established"

Section 16 - OTHER INFORMATION

LIMITED EVIDENCE

- Cumulative effects may result following exposure*.
- * (limited evidence).

Denmark Advisory list for selfclassification of dangerous substances

Substance CAS Suggested codes hydrogen sulfide 7783- 06- 4 N R50

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- Classification of the mixture and its individual components has drawn on official and authoritative sources as well as independent review by the Chemwatch Classification committee using available literature references.

A list of reference resources used to assist the committee may be found at:
www.chemwatch.net/references.

- The (M)SDS is a Hazard Communication tool and should be used to assist in the Risk Assessment. Many factors determine whether the reported Hazards are Risks in the workplace or other settings. Risks may be determined by reference to Exposures Scenarios. Scale of use, frequency of use and current or available engineering controls must be considered.

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