

1,4-Phenylenediamine

sc-237769



The Power is Question

Material Safety Data Sheet

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

Section 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

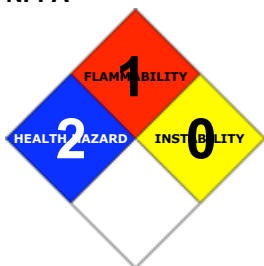
PRODUCT NAME

1,4-Phenylenediamine

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 United States of America

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

Azo dye intermediate, photographic developing agent, photochemical measurements, intermediate in manufacture of antioxidants and accelerators for rubber, synthetic fibres, laboratory reagent, dyeing hair and fur. Intermediate

SYNONYMS

C6-H8-N2, C6H4(NH2)2, p-aminoaniline, "Durafur Black R", 4-aminoaniline, "Fouramine D", p-benzenediamine, "Fourrine D", "phenylene diamine", "1, 4-benzenediamine", "Fourrine 1", "1, 4-diaminobenzene", "Fur Black 41867", "1, 4-phenylenediamine", "Fur Brown 41866", PPD, "Furro D", "BASF Ursol D", "Fur Yellow", "Benzofur D", "Futramine D", "C.I. 76060", "Nako H", "Cl 76060", Orsin, Cl76060, "Oxidation Base 10", "C.I. Developer 13", Pelagol, "C.I. Oxidation Base 10", Peltol, "Developer 13", phenylenediamines

Section 2 - HAZARDS IDENTIFICATION

CHEMWATCH 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



CANADIAN WHMIS SYMBOLS



EMERGENCY OVERVIEW

RISK

Irritating to eyes.

May cause SENSITIZATION by skin contact.

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

Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

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.

■ Systemic effects of p-phenylenediamine include asthma, gastritis (regardless of portal of entry), rises in blood pressure, transudation in serous cavities, vertigo, tremors, convulsions, and coma. Single oral doses of p-phenylenediamine can produce kidney failure. One reported case(1) study cites the development of optic atrophy with resultant blindness which persisted in a follow-up 6 months later. The dose was estimated to be 7 gm. The patient was acutely asphyxiated with a swollen oedematous face and neck and his eyes protruded (exophthalmos). Symptoms had resolved within three days after extensive steroid treatment but optic atrophy remained.

Yagi H., et al: Human and Experimental Toxicology, 1996, 15, 617-618

Single oral doses cause oedema of the head in animals (especially in rabbits) and damage muscle fibres in rats.

Methaemoglobin formation has been seen only in rats.

Rhabdomyolysis (muscle disintegration with excretion of myoglobin in the blood) is the principal mechanism underlying p-phenylenediamine systemic toxicity. It is particularly responsible for renal failure.

EYE

■ This material can cause eye irritation and damage in some persons.

■ Irritation of the eyes may produce a heavy secretion of tears (lachrymation).

SKIN

■ Skin contact with the material may produce toxic effects; systemic effects may result following absorption.

■ There is some evidence to suggest that the material may cause moderate inflammation of the skin either following direct contact or after a delay of some time. Repeated exposure can cause contact dermatitis which is characterized by redness, swelling and blistering.

■ Molten material is capable of causing burns.

■ 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 vapors or aerosols (mists, fumes), generated by the material during the course of normal handling, may produce toxic effects.

■ There is some evidence to suggest that the material can cause respiratory irritation in some persons. The body's response to such irritation can cause further lung damage.

■ Persons with impaired respiratory function, airway diseases and conditions such as emphysema or chronic bronchitis, may incur further disability if excessive concentrations of particulate are inhaled.

■ Processing for an overly long time or processing at overly high temperatures may cause generation and release of highly irritating vapors, which irritate eyes, nose, throat, causing red itching eyes, coughing, sore throat.

■ Usually handled as molten liquid which requires worker thermal protection and increases hazard of vapor exposure. CAUTION: Vapors may be irritating.

CHRONIC HEALTH EFFECTS

■ Skin contact with the material is more likely to cause a sensitization reaction in some persons compared to the general population.

There has been some concern that this material can cause cancer or mutations but there is not enough data to make an assessment.

Limited evidence suggests that repeated or long-term occupational exposure may produce cumulative health effects involving organs or biochemical systems.

There is some evidence that inhaling this product is more likely to cause a sensitization reaction in some persons compared to the general population.

p-Phenylenediamine is suspected as a cause of bladder cancers in "aniline" workers.

Long term exposure to p-phenylenediamine may produce mucosal irritation, asthma, oedema and liver damage. "Ursol" asthma and persistent irritation of the upper airways of workers in the fur industry has been described. In 30% of workers employed in the dying of skins, p-phenylenediamine caused skin lesions, eczematous rashes, irritation of the upper respiratory tract and occasional asthma attacks. One skin dyer developed severe bronchial asthma after working with "Ursol" for one year; the asthma attacks always developed half an hour after work. Long term dermal exposure to

p-phenylenediamine in hair dyes caused such severe damage of the kidneys and other organs that it resulted in the more or less rapid death of several persons.

In vitro, after metabolic activation, p-phenylenediamine is mutagenic; in the Ames test the mutagenicity is increased by the addition of hydrogen peroxide (a chemical commonly used by hair dressers). There is no evidence that p-phenylenediamine has embryotoxic or teratogenic potential. Present data does not dispel the suspicion that p-phenylenediamine has carcinogenic potential.

Phenylenediamine derivatives can cause skin damage, which generally disappears when exposure ceases.

Most arylamines are powerful poisons to the blood-making system. High chronic doses cause congestion of the spleen and tumor formation.

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
p-phenylenediamine	106-50-3	> 99

Section 4 - FIRST AID MEASURES

SWALLOWED

- Give a slurry of activated charcoal in water to drink. NEVER GIVE AN UNCONSCIOUS PATIENT WATER TO DRINK.
- At least 3 tablespoons in a glass of water should be given.
- Although induction of vomiting may be recommended (IN CONSCIOUS PERSONS ONLY), such a first aid measure is dissuaded because to the risk of aspiration of stomach contents. (i) It is better to take the patient to a doctor who can decide on the necessity and method of emptying the stomach. (ii) Special circumstances may however exist; these include non- availability of charcoal and the ready availability of the doctor.

NOTE: If vomiting is induced, lean patient forward or place on left side (head-down position, if possible) to maintain open airway and prevent aspiration. NOTE: Wear protective gloves when inducing vomiting.

- REFER FOR MEDICAL ATTENTION WITHOUT DELAY.
- In the mean time, qualified first-aid personnel should treat the patient following observation and employing supportive measures as indicated by the patient's condition.
- If the services of a medical officer or medical doctor are readily available, the patient should be placed in his/her care and a copy of the MSDS should be provided. Further action will be the responsibility of the medical specialist.
- If medical attention is not available on the worksite or surroundings send the patient to a hospital together with a copy of the MSDS.

(ICSC20305/20307).

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.

For THERMAL burns:

- Do NOT remove contact lens
- Lay victim down, on stretcher if available and pad BOTH eyes, make sure dressing does not press on the injured eye by placing thick pads under dressing, above and below the eye.
- Seek urgent medical assistance, or transport to hospital.

SKIN

■ If skin or hair contact occurs:

- Quickly but gently, wipe material off skin with a dry, clean cloth.
- Immediately 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.

In case of burns:

- Immediately apply cold water to burn either by immersion or wrapping with saturated clean cloth.
- DO NOT remove or cut away clothing over burnt areas. DO NOT pull away clothing which has adhered to the skin as this can cause further injury.
- DO NOT break blister or remove solidified material.
- Quickly cover wound with dressing or clean cloth to help prevent infection and to ease pain.
- For large burns, sheets, towels or pillow slips are ideal; leave holes for eyes, nose and mouth.
- DO NOT apply ointments, oils, butter, etc. to a burn under any circumstances.
- Water may be given in small quantities if the person is conscious.
- Alcohol is not to be given under any circumstances.
- Reassure.
- Treat for shock by keeping the person warm and in a lying position.
- Seek medical aid and advise medical personnel in advance of the cause and extent of the injury and the estimated time of arrival of the patient.

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.

NOTES TO PHYSICIAN

■ Treat symptomatically.

for poisons (where specific treatment regime is absent):

BASIC TREATMENT

- Establish a patent airway with suction where necessary.
- Watch for signs of respiratory insufficiency and assist ventilation as necessary.
- Administer oxygen by non-rebreather mask at 10 to 15 l/min.
- Monitor and treat, where necessary, for pulmonary edema .
- Monitor and treat, where necessary, for shock.
- Anticipate seizures .
- DO NOT use emetics. Where ingestion is suspected rinse mouth and give up to 200 ml water (5 ml/kg recommended) for dilution where patient is able to swallow, has a strong gag reflex and does not drool.

ADVANCED TREATMENT

- Consider orotracheal or nasotracheal intubation for airway control in unconscious patient or where respiratory arrest has occurred.
- Positive-pressure ventilation using a bag-valve mask might be of use.
- Monitor and treat, where necessary, for arrhythmias.
- Start an IV D5W TKO. If signs of hypovolemia are present use lactated Ringers solution. Fluid overload might create complications.
- Drug therapy should be considered for pulmonary edema.
- Hypotension with signs of hypovolemia requires the cautious administration of fluids. Fluid overload might create complications.
- Treat seizures with diazepam.
- Proparacaine hydrochloride should be used to assist eye irrigation.

BRONSTEIN, A.C. and CURRANCE, P.L.

EMERGENCY CARE FOR HAZARDOUS MATERIALS EXPOSURE: 2nd Ed. 1994.

Wherever histamine-like effects predominate, a therapeutic trial with an antihistaminic is suggested. Not likely to induce significant methaemoglobinaemia.

Section 5 - FIRE FIGHTING MEASURES

Vapour Pressure (mmHG):	Very low @ 20 C
Upper Explosive Limit (%):	Not available.
Specific Gravity (water=1):	>1
Lower Explosive Limit (%):	Not available.

EXTINGUISHING MEDIA

- Do NOT direct a solid stream of water or foam into burning molten material; this may cause spattering and spread the fire.
- 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 solid which burns but propagates flame with difficulty.
- Avoid generating dust, particularly clouds of dust in a confined or unventilated space as dusts may form an explosive mixture with air, and any source of ignition, i.e. flame or spark, will cause fire or explosion. Dust clouds generated by the fine grinding of the solid are a particular hazard; accumulations of fine dust may burn rapidly and fiercely if ignited.
- Dry dust can be charged electrostatically by turbulence, pneumatic transport, pouring, in exhaust ducts and during transport.
- Build-up of electrostatic charge may be prevented by bonding and grounding.
- Powder handling equipment such as dust collectors, dryers and mills may require additional protection measures such as explosion venting.

Combustion products include: carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x), other pyrolysis products typical of burning organic material.

May emit poisonous fumes.

CARE: Contamination of heated / molten liquid with water may cause violent steam explosion, with scattering of hot contents.

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.

Gloves:

Respirator:

Type AK-P Filter of sufficient capacity

Section 6 - ACCIDENTAL RELEASE MEASURES

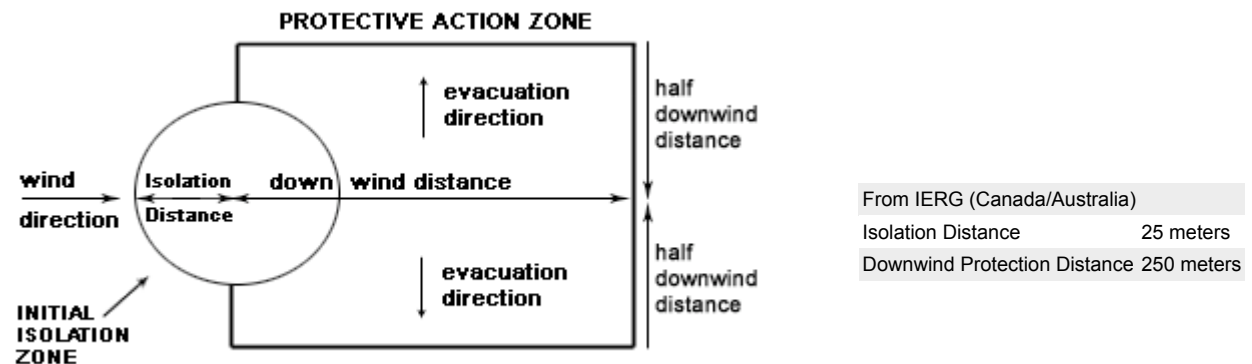
MINOR SPILLS

- Clean up waste regularly and abnormal spills immediately.
- Avoid breathing dust and contact with skin and eyes.
- Wear protective clothing, gloves, safety glasses and dust respirator.
- Use dry clean up procedures and avoid generating dust.
- Vacuum up or sweep up. NOTE: Vacuum cleaner must be fitted with an exhaust micro filter (HEPA type) (consider explosion-proof machines designed to be grounded during storage and use).
- Dampen with water to prevent dusting before sweeping.
- Place in suitable containers for disposal.

MAJOR SPILLS

- 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.
- 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



From US Emergency Response Guide 2000 Guide 153

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.

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 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.

Section 7 - HANDLING AND STORAGE

PROCEDURE FOR HANDLING



- The greatest potential for injury caused by molten materials occurs during purging of machinery (moulders, extruders etc.)
- It is essential that workers in the immediate area of the machinery wear eye and skin protection (such as full face, safety glasses, heat resistant gloves, overalls and safety boots) as protection from thermal burns.
- Fumes or vapors emitted from hot melted materials, during converting operations, may condense on overhead metal surfaces or exhaust ducts. The condensate may contain substances which are irritating or toxic. Avoid contact of that material with the skin. Wear rubber or other impermeable gloves when cleaning contaminated areas.
- Avoid process temperatures above decomposition temperatures. Overheating may occur at excessively high cylinder heats, overworking of the melt by wrong screw configuration, or by long dwell time in the machine. Under such conditions, thermal emissions and heat-degradation products might, without proper ventilation, reach hazardous concentrations in the converting area. Hot purgings should be collected only as thin flat strands to allow for rapid cooling. Hot purgings should be cooled by quenching in water in a well-ventilated area.
- Avoid all personal contact, including inhalation.
- Wear protective clothing when risk of exposure occurs.
- Use in a well-ventilated area.
- Prevent concentration in hollows and sumps.
- DO NOT enter confined spaces until atmosphere has been checked.
- DO NOT allow material to contact humans, exposed food or food utensils.
- 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.

Empty containers may contain residual dust which has the potential to accumulate following settling. Such dusts may explode in the presence of an appropriate ignition source.

- Do NOT cut, drill, grind or weld such containers.
- In addition ensure such activity is not performed near full, partially empty or empty containers without appropriate workplace safety authorisation or permit.

RECOMMENDED STORAGE METHODS

■ 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.

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.

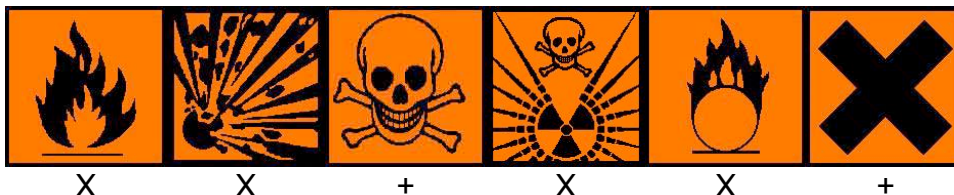
- Where combination packages are used, and the inner packages are of glass, there must be sufficient inert cushioning material in contact

with inner and outer packages * . - In addition, where inner packagings are glass and contain liquids of packing group I and II there must be sufficient inert absorbent to absorb any spillage *. - * 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
Canada - British Columbia Occupational Exposure Limits	p-phenylenediamine (p-Phenylenediamine)		0.1						S
Canada - Ontario Occupational Exposure Limits	p-phenylenediamine (p-Phenylenediamine)		0.1						Skin
Canada - Alberta Occupational Exposure Limits	p-phenylenediamine (p-Phenylenediamine)		0.1						
US ACGIH Threshold Limit Values (TLV)	p-phenylenediamine (p-Phenylenediamine)		0.1						TLV Basis: upper respiratory tract irritation; skin sensitization
US NIOSH Recommended Exposure Limits (RELs)	p-phenylenediamine (p-Phenylene diamine)		0.1						[skin]
US - Minnesota Permissible Exposure Limits (PELs)	p-phenylenediamine (p-Phenylene diamine)		0.1						
US - Vermont Permissible Exposure Limits Table Z-1-A Transitional Limits for Air Contaminants	p-phenylenediamine (p-Phenylene diamine)		0.1						
US - Vermont Permissible Exposure Limits Table Z-1-A Final Rule Limits for Air Contaminants	p-phenylenediamine (p-Phenylene diamine)		0.1						
US - Tennessee Occupational Exposure Limits - Limits For Air Contaminants	p-phenylenediamine (p-Phenylene diamine)		0.1						
US - California Permissible Exposure Limits for Chemical Contaminants	p-phenylenediamine (p-Phenylenediamine)		0.1						
US - Idaho - Limits for Air Contaminants	p-phenylenediamine (p-Phenylene diamine)		0.1						
US OSHA Permissible Exposure Levels (PELs) - Table Z1	p-phenylenediamine (p-Phenylene diamine)		0.1						

US - Alaska Limits for Air Contaminants	p-phenylenediamine (p-Phenylene diamine)	0.1		
US - Michigan Exposure Limits for Air Contaminants	p-phenylenediamine (p-Phenylenediamine)	0.1		
US - Hawaii Air Contaminant Limits	p-phenylenediamine (p-Phenylene diamine)	0.1		
Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances	p-phenylenediamine (p-Phenylene diamine - Skin)	0.1	0.1	
US - Washington Permissible exposure limits of air contaminants	p-phenylenediamine (p-Phenylene diamine)	0.1	0.3	
US - Oregon Permissible Exposure Limits (Z-1)	p-phenylenediamine (p-Phenylene diamine)	0.1		
US - Wyoming Toxic and Hazardous Substances Table Z1 Limits for Air Contaminants	p-phenylenediamine (p-Phenylene diamine)	0.1		
Canada - Quebec Permissible Exposure Values for Airborne Contaminants (English)	p-phenylenediamine (para-Phenylenediamine)	0.1		
Canada - Prince Edward Island Occupational Exposure Limits	p-phenylenediamine (p-Phenylenediamine)	0.1		TLV Basis: upper respiratory tract irritation; skin sensitization
Canada - Northwest Territories Occupational Exposure Limits (English)	p-phenylenediamine (p-Phenylene diamine - Skin)	0.1	0.3	
Canada - Nova Scotia Occupational Exposure Limits	p-phenylenediamine (p-Phenylenediamine)	0.1		TLV Basis: upper respiratory tract irritation; skin sensitization
Canada - Saskatchewan Occupational Health and Safety Regulations - Contamination Limits	p-phenylenediamine (Phenylene diamine isomers)	0.1	0.3	

EMERGENCY EXPOSURE LIMITS

Material	p-phenylenediamine
Original IDLH Value (ppm)	

MATERIAL DATA

P-PHENYLENEDIAMINE:

■ for p-phenylenediamine:

p-Phenylenediamine is a known dermal and possible respiratory sensitizer in humans and cause local dermatitis, urticaria, asthma and inflammatory reactions of the respiratory tract. Lachrymation, ophthalmia and permanent blindness after eye contact have been described.

Topical applications of (oxidised) p-phenylenediamine to rats has produced local skin tumours at the site of application or may cause tumours distant from the site, especially of the mammary gland of female rats.

Exposure at or below the recommended level is thought to provide protection from respiratory and skin sensitisation and to protect against blood dyscrasia and excess risk of occupational cancer. Even though this limit may be sufficiently low to minimise the number of people who may become sensitised it may not be low enough to prevent exacerbation of

pre-existing asthma. A skin notation was deleted in 1991 because there was no definitive data to demonstrate that absorption of the substance through the skin produced systemic damage.

PERSONAL PROTECTION



Consult your EHS staff for recommendations

EYE

-
- Safety glasses with side shields.
- Chemical goggles.

- Contact lenses pose a special hazard; soft lenses may absorb irritants and all lenses concentrate them. DO NOT wear contact lenses.

HANDS/FEET

■ Wear chemical protective gloves, eg. PVC.
Wear safety footwear or safety gumboots, eg. Rubber.

NOTE: The material may produce skin sensitization in predisposed individuals. Care must be taken, when removing gloves and other protective equipment, to avoid all possible skin contact.

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.

- When handling hot materials wear heat resistant, elbow length gloves.
- Rubber gloves are not recommended when handling hot objects, materials
- Protective gloves eg. Leather gloves or gloves with Leather facing

OTHER

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

Usually handled as molten liquid which requires worker thermal protection and increases hazard of vapor exposure. CAUTION: Vapors may be irritating.

- Overalls.
- Eyewash unit.
- Barrier cream.
- Skin cleansing cream.

RESPIRATOR

- Respirators may be necessary when engineering and administrative controls do not adequately prevent exposures.
- The decision to use respiratory protection should be based on professional judgment that takes into account toxicity information, exposure measurement data, and frequency and likelihood of the worker's exposure - ensure users are not subject to high thermal loads which may result in heat stress or distress due to personal protective equipment (powered, positive flow, full face apparatus may be an option).
- Published occupational exposure limits, where they exist, will assist in determining the adequacy of the selected respiratory . These may be government mandated or vendor recommended.
- Certified respirators will be useful for protecting workers from inhalation of particulates when properly selected and fit tested as part of a complete respiratory protection program.
- Use approved positive flow mask if significant quantities of dust becomes airborne.
- Try to avoid creating dust conditions.

RESPIRATOR

Protection Factor	Half-Face Respirator	Full-Face Respirator	Powered Air Respirator
10 x PEL	AK P1	-	AK PAPR-P1
	Air-line*	-	-
50 x PEL	Air-line**	AK P2 AK	PAPR-P2
100 x PEL	-	AK P3	-
		Air-line*	-
100+ x PEL	-	Air-line**	AK PAPR-P3

* - Negative pressure demand ** - Continuous flow

Explanation of Respirator Codes:

Class 1 low to medium absorption capacity filters.

Class 2 medium absorption capacity filters.

Class 3 high absorption capacity filters.

PAPR Powered Air Purifying Respirator (positive pressure) cartridge.

Type A for use against certain organic gases and vapors.

Type AX for use against low boiling point organic compounds (less than 65°C).

Type B for use against certain inorganic gases and other acid gases and vapors.

Type E for use against sulfur dioxide and other acid gases and vapors.

Type K for use against ammonia and organic ammonia derivatives

Class P1 intended for use against mechanically generated particulates of sizes most commonly encountered in industry, e.g. asbestos, silica.

Class P2 intended for use against both mechanically and thermally generated particulates, e.g. metal fume.

Class P3 intended for use against all particulates containing highly toxic materials, e.g. beryllium.

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

■ For molten materials:

Provide mechanical ventilation; in general such ventilation should be provided at compounding/ converting areas and at fabricating/ filling work stations where the material is heated. Local exhaust ventilation should be used over and in the vicinity of machinery involved in handling the molten material.

- Local exhaust ventilation is required where solids are handled as powders or crystals; even when particulates are relatively large, a certain proportion will be powdered by mutual friction.
- Exhaust ventilation should be designed to prevent accumulation and recirculation of particulates in the workplace.
- If in spite of local exhaust an adverse concentration of the substance in air could occur, respiratory protection should be considered. Such protection might consist of:

(a): particle dust respirators, if necessary, combined with an absorption cartridge;

(b): filter respirators with absorption cartridge or canister of the right type;

(c): fresh-air hoods or masks

- Build-up of electrostatic charge on the dust particle, may be prevented by bonding and grounding.
- Powder handling equipment such as dust collectors, dryers and mills may require additional protection measures such as explosion venting.

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

Type of Contaminant:	Air Speed:
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.)
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 4-10 m/s (800-2000 f/min) for extraction of crusher dusts generated 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

Solid.

Does not mix with water.

Sinks in water.

State	Divided solid	Molecular Weight	108.16
Melting Range (°F)	285.8- 296.6	Viscosity	Not Applicable
Boiling Range (°F)	512.6	Solubility in water (g/L)	Partly miscible
Flash Point (°F)	311	pH (1% solution)	Not applicable
Decomposition Temp (°F)	Not Available	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not available.	Vapour Pressure (mmHG)	Very low @ 20 C
Upper Explosive Limit (%)	Not available.	Specific Gravity (water=1)	>1
Lower Explosive Limit (%)	Not available.	Relative Vapor Density (air=1)	3.71
Volatile Component (%vol)	Not available	Evaporation Rate	Not available

APPEARANCE

White to light purple crystals or powder. Oxidises on standing in air to purple and black. Affected by light. Soluble in alcohol, ether and 100 parts water. Bulk shipments are molten. Presence of unreacted material in rubber accelerators has caused sensitisation, allergic responses.

Section 10 - CHEMICAL STABILITY

CONDITIONS CONTRIBUTING TO INSTABILITY



- Presence of incompatible materials.
- Product is considered stable.
- Hazardous polymerization will not occur.

STORAGE INCOMPATIBILITY



- Many arylamines (aromatic amines such as aniline, N-ethylaniline, o-toluidine, xylydine etc. and their mixtures) are hypergolic (ignite spontaneously) with red fuming nitric acid. When the amines are dissolved in triethylamine, ignition occurs at -60 deg. C. or less.
- Various metal oxides and their salts may promote ignition of amine-red fuming nitric acid systems. Soluble materials such as copper(II) oxide, ammonium metavanadate are effective; insoluble materials such as copper(II) oxide, iron(II) oxide, potassium dichromate are also effective.
- Avoid oxidizing agents, acids, acid chlorides, acid anhydrides.

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

Section 11 - TOXICOLOGICAL INFORMATION

P-PHENYLENEDIAMINE

TOXICITY AND IRRITATION

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

TOXICITY	IRRITATION
Oral (rat) LD50: 80 mg/kg	Skin (human): 250 mg/24h
Dermal (rabbit) LDLo: 5000 mg/kg	Skin (rabbit): 12.5 mg/24h - Mild
	Skin (rabbit):250 mg/24h-Moderate

■ Contact allergies quickly manifest themselves as contact eczema, more rarely as urticaria or Quincke's edema. The pathogenesis of contact eczema involves a cell-mediated (T lymphocytes) immune reaction of the delayed type. Other allergic skin reactions, e.g. contact urticaria, involve antibody-mediated immune reactions. The significance of the contact allergen is not simply determined by its sensitization potential: the distribution of the substance and the opportunities for contact with it are equally important. A weakly sensitizing substance which is widely distributed can be a more important allergen than one with stronger sensitizing potential with which few individuals come into contact. From a clinical point of view, substances are noteworthy if they produce an allergic test reaction in more than 1% of the persons tested.

p-Phenylenediamines are oxidised by the liver microsomal enzymes (S9). Pure p-phenylenediamine is non-mutagenic in but becomes mutagenic after it is oxidized. Azo dyes containing phenylenediamine are mutagenic in certain assay most likely due to the formation of oxidized p-phenylenediamine. Modification of the moieties that can be metabolized to p-phenylenediamine by sulfonation, carboxylation or copper complexation eliminated the mutagenic responses.

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.

The substance is classified by IARC as Group 3:

NOT classifiable as to its carcinogenicity to humans.

Evidence of carcinogenicity may be inadequate or limited in animal testing.

CARCINOGEN

para-Phenylenediamine	International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs	Group	3
p-Phenylenediamine	ND	Carcinogen Category	A4
SKIN			
p-phenylenediamine	ND	Notes	Skin
p-phenylenediamine	ND	Skin	Yes
p-phenylenediamine	US - Tennessee Occupational Exposure Limits - Limits For Air Contaminants - Skin	Skin Designation	X
p-phenylenediamine	US - Vermont Permissible Exposure Limits Table Z-1-A Transitional Limits for Air Contaminants - Skin	Skin Designation	X
p-phenylenediamine	US - Vermont Permissible Exposure Limits Table Z-1-A Final Rule Limits for Air Contaminants - Skin	Skin Designation	X
p-phenylenediamine	US - Washington Permissible exposure limits of air contaminants - Skin	Skin	X
p-phenylenediamine	US - Minnesota Permissible Exposure Limits (PELs) - Skin	Skin Designation	X
p-phenylenediamine	US - Hawaii Air Contaminant Limits - Skin Designation	Skin Designation	X

p-phenylenediamine ND	Skin Designation	X
p-phenylenediamine US OSHA Permissible Exposure Levels (PELs) - Skin	Skin Designation	X
p-phenylenediamine ND	Skin	X
p-phenylenediamine US - California Permissible Exposure Limits for Chemical Contaminants - Skin	Skin	X
p-phenylenediamine US - California Permissible Exposure Limits for Chemical Contaminants - Skin	Skin	S

Section 12 - ECOLOGICAL INFORMATION

Refer to data for ingredients, which follows:

P-PHENYLENEDIAMINE:

Marine Pollutant:	Yes
■ Hazardous Air Pollutant:	Yes
■ Fish LC50 (96hr.) (mg/l):	5.74 (48hr)
■ Half- life Soil - High (hours):	672
■ Half- life Soil - Low (hours):	168
■ Half- life Air - High (hours):	2.8
■ Half- life Air - Low (hours):	0.28
■ Half- life Surface water - High (hours):	672
■ Half- life Surface water - Low (hours):	31
■ Half- life Ground water - High (hours):	1344
■ Half- life Ground water - Low (hours):	336
■ Aqueous biodegradation - Aerobic - High (hours):	672
■ Aqueous biodegradation - Aerobic - Low (hours):	168
■ Aqueous biodegradation - Anaerobic - High (hours):	2688
■ Aqueous biodegradation - Anaerobic - Low (hours):	672
■ Photolysis maximum light absorption - High (nano- m):	308
■ Photooxidation half- life water - High (hours):	1740
■ Photooxidation half- life water - Low (hours):	31
■ Photooxidation half- life air - High (hours):	2.8
■ Photooxidation half- life air - Low (hours):	0.28

■ Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

■ 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.

■ Phenylenediamines are not readily biodegradable via CO2 evolution, but they are susceptible to both hydrolysis and photodegradation. These materials have been shown not to partition to water or air if released into the environment due to their low water solubility and low vapor pressure. Analytical studies of hydrolysis products indicate that the molecule cleaves at the aromatic carbon-nitrogen bond.

It is difficult to define clearly the ways in which phenylenediamines are eliminated from the hydrosphere. Elimination processes such as oxidation reactions, adsorption, and stripping effects can only be conjectured. It is impossible to say with any degree of certainty for any of the three isomers what proportion of their elimination is accounted for by biodegradation. The following elimination rates have been found: between 0 and 69 % for o-phenylenediamine, between 0 and 60 % for m-phenylenediamine and between 0 and 100 % for p-phenylenediamine. It is assumed that any phenylenediamines released into the atmosphere are destroyed by photodegradation. The calculated half-life is less than 2 hours. The low POW values indicate that bioaccumulation is unlikely to occur to any significant degree. Only one study has dealt with the behaviour of phenylenediamines in soil, in respect to their soil sorption and geoaccumulation. According to this study, adsorption is relatively strong at low concentrations and expandable clay minerals but quite weak at higher concentrations. No information is available on the sorption behaviour against organic material.

The substituted p-phenylenediamines and presumably the other isomers, in general, are very toxic to aquatic organisms.

■ Aromatic amines (arylamines), particularly primary aromatic amines, covalently and irreversibly bind to humic substances present in most natural waters.

All metabolites with moieties of: anilines, benzidines and toluidines are of environmental concern. Anilines and benzidines are both acutely toxic and toxic depending on the specific aquatic species (except algae). Toluidines represent a similar concern. It has been speculated that aqueous solutions of aromatic amines can be oxidised by organic radicals, but there are no actual data on reaction rates. Based on a study of reaction rate data for these compounds an estimate of the half-life of aromatic amines in water is approximately 100 days, assuming a peroxy radical concentration of 10⁻¹⁰ mole/L in sunlit, oxygenated water.

■ DO NOT discharge into sewer or waterways.

Toxicity Fish: LC50(48)5.74mg/L

Bioaccumulation: not sig

Degradation Biological: by soil microflora >64 days

Ecotoxicity

Ingredient
p-phenylenediamine

Persistence: Water/Soil
LOW

Persistence: Air
LOW

Bioaccumulation
LOW

Mobility
HIGH

Section 13 - DISPOSAL CONSIDERATIONS

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. 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.
- Dispose of by: Burial in a licensed land-fill or Incineration in a licensed apparatus (after admixture with suitable combustible material)
- Decontaminate empty containers. Observe all label safeguards until containers are cleaned and destroyed.

Section 14 - TRANSPORTATION INFORMATION



DOT:

Symbols:	+	Hazard class or Division:	6.1
Identification Numbers:	UN1673	PG:	III
Label Codes:	6.1	Special provisions:	IB8, IP3, T1, TP33
Packaging: Exceptions:	153	Packaging: Non-bulk:	213
Packaging: Exceptions:	153	Quantity limitations: Passenger aircraft/rail:	100 kg
Quantity Limitations: Cargo aircraft only:	200 kg	Vessel stowage: Location:	A
Vessel stowage: Other:	None		

Hazardous materials descriptions and proper shipping names:

Phenylenediamines (o-; m-; p-;)

Air Transport IATA:

ICAO/IATA Class:	6.1	ICAO/IATA Subrisk:	None
UN/ID Number:	1673	Packing Group:	III
Special provisions:	A113		

Shipping Name: PHENYLENEDIAMINES

Maritime Transport IMDG:

IMDG Class:	6.1	IMDG Subrisk:	None
UN Number:	1673	Packing Group:	III
EMS Number:	F-A, S-A	Special provisions:	279
Limited Quantities:	5 kg	Marine Pollutant:	Yes

Shipping Name: PHENYLENEDIAMINES

Section 15 - REGULATORY INFORMATION



REGULATIONS

p-phenylenediamine (CAS: 106-50-3) is found on the following regulatory lists;

"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 - Prince Edward Island Occupational Exposure Limits - Carcinogens", "Canada - Quebec Permissible Exposure Values for Airborne Contaminants (English)", "Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances", "Canada Domestic Substances List (DSL)", "Canada Ingredient Disclosure List (SOR/88-64)", "International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs", "International Council of Chemical 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 Permissible Exposure Limits for Chemical Contaminants", "US - California Toxic Air Contaminant List Category IV", "US - Connecticut Hazardous Air Pollutants", "US - Hawaii Air Contaminant Limits", "US - Idaho - Limits for Air Contaminants", "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 Permissible Exposure Limits (Z-1)", "US - Pennsylvania - Hazardous Substance List", "US - Rhode Island Hazardous Substance List", "US - Tennessee Occupational Exposure Limits - Limits For Air Contaminants", "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 Permissible exposure limits of air contaminants", "US - Wyoming Toxic and Hazardous Substances Table Z1 Limits for Air Contaminants", "US ACGIH Threshold Limit Values (TLV)", "US ACGIH Threshold Limit Values (TLV) - Carcinogens", "US CAA (Clean Air Act) - HON Rule - Organic HAPs (Hazardous Air Pollutants)", "US Clean Air Act - Hazardous Air Pollutants", "US Cosmetic Ingredient Review (CIR) Cosmetic ingredients found safe as used", "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 High Production Volume Program Chemical List", "US EPA Master Testing List - Index I Chemicals Listed", "US EPCRA Section 313 Chemical List", "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 499 Combustible Dusts", "US NIOSH Recommended Exposure Limits (RELs)", "US OSHA Permissible Exposure Levels (PELs) - Table Z1", "US RCRA (Resource Conservation & Recovery Act) - Appendix IX to Part 264 Ground-Water Monitoring List 1", "US RCRA (Resource Conservation & Recovery Act) - List of Hazardous Inorganic and Organic Constituents 1", "US Toxic Substances Control Act (TSCA) - Inventory", "US TSCA Section 4/12 (b) - Sunset Date/Status", "US TSCA Section 8 (d) - Health and Safety Data Reporting"

Section 16 - OTHER INFORMATION

LIMITED EVIDENCE

- Cumulative effects may result following exposure*.
- May produce discomfort of the respiratory system and skin*.
- Limited evidence of a carcinogenic effect*.
- Possible respiratory sensitizer*.

* (limited evidence).

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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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