

MANGANESE DIOXIDE

GHS Safety Data Sheet

Version No:6

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Section 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME

MANGANESE DIOXIDE

OTHER NAMES

Mn-O₂, "black manganese oxide", "Bog manganese", Braustein, Bruinstein, "cement black", "manganese black", "manganese peroxide", "manganese dioxide black", "manganese superoxide", pyrolusite, "electrolytic manganese dioxide"

PROPER SHIPPING NAME

OXIDIZING SOLID, N.O.S.(contains manganese dioxide)

PRODUCT USE

The mineral is the source of manganese and all its compounds; largely used in the manufacture of manganese steel; in alkaline batteries (dry cell); for making amethyst glass, decolourising glass. Also used for painting on porcelain, faience and majolica. The solid is used in electrotechnics, pigments, browning gun barrels. Manganese salts are driers for paints and varnishes, printing and dyeing textiles.
Intermediate

SUPPLIER

Company: S D FINE - CHEM LIMITED

Address:

315- 317, T.V.IND.ESTATE,

248 WORLI ROAD,

MUMBAI- 400 030, INDIA

technical@sdfine.com

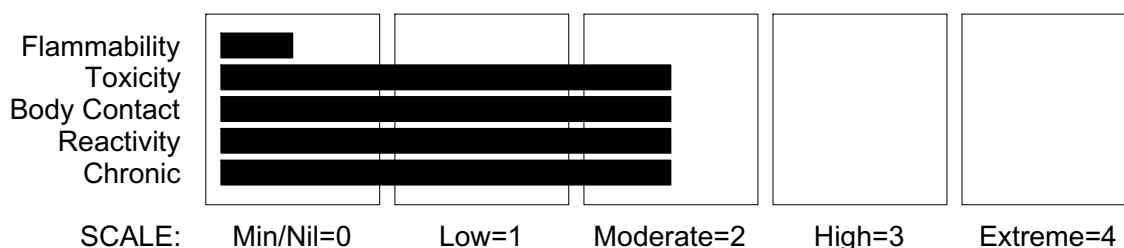
Telephone: 91- 22 24959898

Telephone: 91- 22 24959899

Fax: 91- 22 24937232

Section 2 - HAZARDS IDENTIFICATION

HAZARD RATINGS



GHS Classification

Acute Toxicity (Inhalation) Category 4

Acute Toxicity (Oral) Category 4

Eye Irritation Category 2A

continued...

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Section 2 - HAZARDS IDENTIFICATION

Oxidizing Solid Category 3
Respiratory Irritation Category 3
Skin Corrosion/Irritation Category 3



EMERGENCY OVERVIEW

HAZARD

WARNING

Determined by using GHS criteria:
H335 H272 H302 H332 H316 H319
May cause respiratory irritation
May intensify fire; oxidizer
Harmful if swallowed
Harmful if inhaled
Causes mild skin irritation
Causes serious eye irritation

PRECAUTIONARY STATEMENTS

Prevention

Keep away from heat/sparks/open flames/hot surfaces. - No smoking.
Keep/Store away from clothing and other combustible materials.
Take any precaution to avoid mixing with combustibles.
Avoid breathing dust/fume/gas/mist/vapours/spray.
Wash thoroughly after handling.
Do not eat, drink or smoke when using this product.
Use only outdoors or in a well-ventilated area.
Wear protective gloves/protective clothing/eye protection/face protection.

Response

IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell.
IF INHALED: Remove to fresh air and keep at rest in a position comfortable for breathing.
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Call a POISON CENTER or doctor/physician if you feel unwell.
Rinse mouth.
If skin irritation occurs: Get medical advice/ attention.
If eye irritation persists: Get medical advice/attention.

Storage

Store in a well-ventilated place. Keep container tightly closed.
Store locked up.

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME
manganese dioxide
commercial product may be mixture of
pyrolusite (manganese oxide - (75- 80%))

CAS RN	%
1313-13-9	~80

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Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

cryptomelane (KMn₈O₁₆)
pyrolomelane BaMn₈O₁₆
rhodonite MnSiO₃
lithiophorite (Al, Li)MnO₂(OH)₂
goethite FeO.OH
(total of 20- 25%)
silica crystalline - quartz

14808-60-7

<4

Section 4 - FIRST AID MEASURES

SWALLOWED

- IF SWALLOWED, REFER FOR MEDICAL ATTENTION, WHERE POSSIBLE, WITHOUT DELAY.
 - For advice, contact a Poisons Information Centre or a doctor.
 - Urgent hospital treatment is likely to be needed.
 - 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.
 - Where medical attention is not immediately available or where the patient is more than 15 minutes from a hospital or unless instructed otherwise:
 - INDUCE vomiting with fingers down the back of the throat, ONLY IF CONSCIOUS. Lean patient forward or place on left side (head-down position, if possible) to maintain open airway and prevent aspiration.
- NOTE: Wear a protective glove when inducing vomiting by mechanical means.

EYE

- If this product comes in contact with the eyes:
- Wash out immediately with fresh 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.
- Seek medical attention without delay; if pain persists or recurs seek medical attention.
- Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

SKIN

- If skin contact occurs:
- Immediately remove all contaminated clothing, including footwear.
- Flush skin and hair with running water (and soap if available).
- Seek medical attention in event of irritation.

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.

NOTES TO PHYSICIAN

- Treat symptomatically.
- Both dermal and oral toxicity of manganese salts is low because of limited solubility of manganese. No known permanent pulmonary sequelae develop after acute manganese exposure. Treatment is supportive.

[Ellenhorn and Barceloux: Medical Toxicology]

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Section 4 - FIRST AID MEASURES

In clinical trials with miners exposed to manganese-containing dusts, L-dopa relieved extrapyramidal symptoms of both hypo kinetic and dystonic patients. For short periods of time symptoms could also be controlled with scopolamine and amphetamine. BAL and calcium EDTA prove ineffective.

[Gosselin et al: Clinical Toxicology of Commercial Products.].

Section 5 - FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA

■ FOR SMALL FIRE:

- USE FLOODING QUANTITIES OF WATER.
- DO NOT use dry chemical, CO₂, foam or halogenated-type extinguishers.

FOR LARGE FIRE:

- Flood fire area with water from a protected position.

FIRE FIGHTING

- Alert Fire Brigade and tell them location and nature of hazard.
- May be violently or explosively reactive.
- Wear breathing apparatus plus protective gloves.
- Prevent, by any means available, spillage from entering drains or water course.
- Fight fire from a safe distance, with adequate cover.
- Extinguishers should be used only by trained personnel.
- Use water delivered as a fine spray to control fire and cool adjacent area.
- Avoid spraying water onto liquid pools.
- 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.
- If fire gets out of control withdraw personnel and warn against entry.
- Equipment should be thoroughly decontaminated after use.

FIRE/EXPLOSION HAZARD

- Will not burn but increases intensity of fire.
 - Heating may cause expansion or decomposition leading to violent rupture of containers.
 - Heat affected containers remain hazardous.
 - Contact with combustibles such as wood, paper, oil or finely divided metal may produce spontaneous combustion or violent decomposition.
 - May emit irritating, poisonous or corrosive fumes.
- Decomposition may produce toxic fumes of: metal oxides.

FIRE INCOMPATIBILITY

- Avoid storage with reducing agents.
- Avoid any contamination of this material as it is very reactive and any contamination is potentially hazardous.

PERSONAL PROTECTION

Glasses:

Full face- shield.

Respirator:

Type AX Filter of sufficient capacity

Section 6 - ACCIDENTAL RELEASE MEASURES

MINOR SPILLS

- Clean up all spills immediately.
- No smoking, naked lights, ignition sources.
- Avoid all contact with any organic matter including fuel, solvents, sawdust, paper or cloth and other incompatible materials, as ignition may result.

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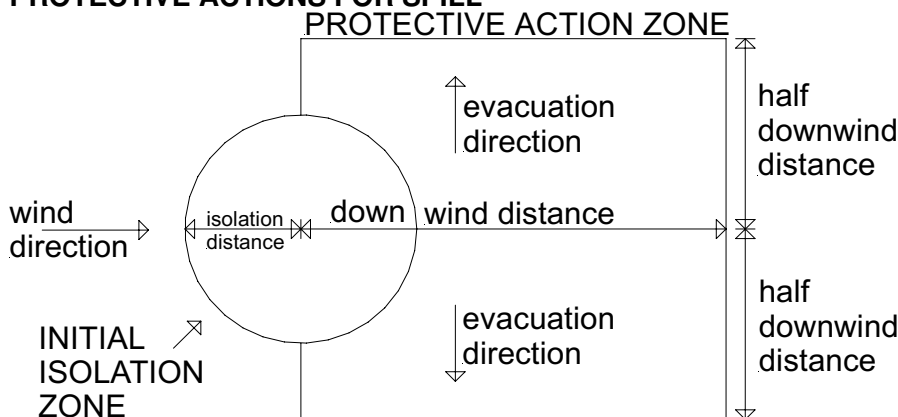
Section 6 - ACCIDENTAL RELEASE MEASURES

- Avoid breathing dust or vapours and all contact with skin and eyes.
- Control personal contact by using protective equipment.
- Contain and absorb spill with dry sand, earth, inert material or vermiculite.
- DO NOT use sawdust as fire may result.
- Scoop up solid residues and seal in labelled drums for disposal.
- Neutralise/decontaminate area.

MAJOR SPILLS

- Clear area of personnel and move upwind.
- Alert Fire Brigade and tell them location and nature of hazard.
- May be violently or explosively reactive.
- Wear full body protective clothing with breathing apparatus.
- Prevent, by any means available, spillage from entering drains or water course.
- Consider evacuation (or protect in place).
- No smoking, flames or ignition sources.
- Increase ventilation.
- Contain spill with sand, earth or other clean, inert materials.
- NEVER use organic absorbents such as sawdust, paper, cloth; as fire may result.
- Avoid any contamination by organic matter.
- Use spark-free and explosion-proof equipment.
- Collect any recoverable product into labelled containers for possible recycling.
- DO NOT mix fresh with recovered material.
- Collect residues and seal in labelled drums for disposal.
- Wash area and prevent runoff into drains.
- Decontaminate equipment and launder all protective clothing before storage and re-use.
- If contamination of drains or waterways occurs advise emergency services.

PROTECTIVE ACTIONS FOR SPILL



From IERG (Canada/Australia)

Isolation Distance	25 metres
Downwind Protection Distance	100 metres
IERG Number	31

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-

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Section 6 - ACCIDENTAL RELEASE MEASURES

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 140 is taken from the US DOT emergency response guide book.

6 IERG information is derived from CANUTEC - Transport Canada.

Personal Protective Equipment advice is contained in Section 8 of the MSDS.

Section 7 - HANDLING AND STORAGE

PROCEDURE FOR HANDLING

- Avoid personal contact and inhalation of dust, mist or vapours.
- Provide adequate ventilation.
- Always wear protective equipment and wash off any spillage from clothing.
- Keep material away from light, heat, flammables or combustibles.
- Keep cool, dry and away from incompatible materials.
- Avoid physical damage to containers.
- DO NOT repack or return unused portions to original containers. Withdraw only sufficient amounts for immediate use.
- Contamination can lead to decomposition leading to possible intense heat and fire.
- When handling NEVER smoke, eat or drink.
- Always wash hands with soap and water after handling.
- Use only good occupational work practice.
- Observe manufacturer's storing and handling directions.

SUITABLE CONTAINER

- DO NOT repack. Use containers supplied by manufacturer only.

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:

- Removable head packaging and
- cans with friction closures 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 moulded plastic box and the substances are not incompatible with the plastic.

STORAGE INCOMPATIBILITY

- **WARNING:** Avoid or control reaction with peroxides. All transition metal peroxides should be considered as potentially explosive. For example transition metal complexes of alkyl hydroperoxides may decompose explosively.
- The pi-complexes formed between chromium(0), vanadium(0) and other transition metals (haloarene-metal complexes) and mono-or poly-fluorobenzene show extreme sensitivity to heat and are explosive.
- Avoid reaction with borohydrides or cyanoborohydrides.
- Avoid storage with reducing agents.
- Inorganic reducing agents react with oxidizing agents to generate heat and products that may be flammable, combustible, or otherwise reactive. Their reactions with oxidizing agents may be violent.
- Incidents involving interaction of active oxidants and reducing agents, either by design or accident, are

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Section 7 - HANDLING AND STORAGE

usually very energetic and examples of so-called redox reactions.

- Inorganic oxidising agents can react with reducing agents to generate heat and products that may be gaseous (causing pressurization of closed containers). The products may themselves be capable of further reactions (such as combustion in the air).
- Organic compounds in general have some reducing power and can in principle react with compounds in this class. Actual reactivity varies greatly with the identity of the organic compound.
- Inorganic oxidising agents can react violently with active metals, cyanides, esters, and thiocyanates.
- Metals and their oxides or salts may react violently with chlorine trifluoride and bromine trifluoride.
- These trifluorides are hypergolic oxidisers. They ignites on contact (without external source of heat or ignition) with recognised fuels - contact with these materials, following an ambient or slightly elevated temperature, is often violent and may produce ignition.
- The state of subdivision may affect the results.

STORAGE REQUIREMENTS

- In addition, Goods of Class 5.1, packing group III should be stored in packages and be separated from buildings, tanks, and compounds containing other dangerous goods in tanks, and from property boundaries by a distance of at least 5 metres.

SAFE STORAGE WITH OTHER CLASSIFIED CHEMICALS



+: May be stored together

O: May be stored together with specific preventions

X: Must not be stored together

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

Source	Material	TWA mg/m ³	Notes
Australia Exposure Standards	manganese dioxide (Silica - Amorphous Fumed silica (respirable dust))	2	(see Chapter 14)
Australia Exposure Standards	silica crystalline - quartz (Silica - Crystalline Quartz)	0.1	(see Chapter 14)
Australia Exposure Standards	silica crystalline - quartz (Silica - Amorphous Fumed silica (respirable dust))	2	(see Chapter 14)

EMERGENCY EXPOSURE LIMITS

Material	Revised IDLH Value (mg/m ³)	Revised IDLH Value (ppm)
manganese dioxide	500	
silica crystalline - quartz	50	

MATERIAL DATA

MANGANESE DIOXIDE:

■ Ceiling values were recommended for manganese and compounds in earlier publications. As manganese is a chronic toxin a TWA is considered more appropriate. Because workers exposed to fume exhibited manganism at air-borne concentrations below those that affect workers exposed to dust a lower value has been proposed to provide an extra margin of safety. This value is still above that experienced by two workers exposed to

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MANGANESE DIOXIDE

manganese fume in the course of one study.

Because the margin of safety of the quartz TLV is not known with certainty and given the associated link between silicosis and lung cancer it is recommended that quartz concentrations be maintained as far below the TLV as prudent practices will allow.

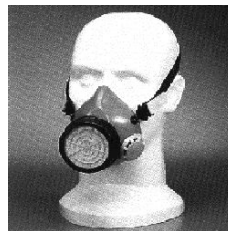
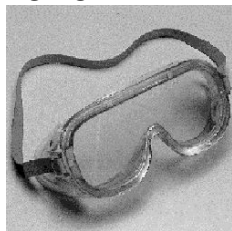
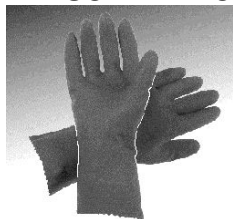
A number of studies have shown that susceptibility to the effects of manganese at or about 1 - 5 mg/m³ (TWA) can lead to clinical manifestations of manganism or more commonly to the development of indicators of sub-clinical manganism (e.g. hand tremor, exaggerated reflexes, short-term memory deficits, poor psychomotor performance). Controlling long-term exposure to the recommended ES TWA level or below should provide protection for those individuals susceptible to neurological effects of prolonged exposure.

SILICA CRYSTALLINE - QUARTZ:

■ The concentration of dust, for application of respirable dust limits, is to be determined from the fraction that penetrates a separator whose size collection efficiency is described by a cumulative log-normal function with a median aerodynamic diameter of 4.0 µm (+-) 0.3 µm and with a geometric standard deviation of 1.5 µm (+-) 0.1 µm, i.e. generally less than 5 µm.

Because the margin of safety of the quartz TLV is not known with certainty and given the associated link between silicosis and lung cancer it is recommended that quartz concentrations be maintained as far below the TLV as prudent practices will allow.

PERSONAL PROTECTION



EYE

- Chemical goggles.
- Full face shield may be required for supplementary but never for primary protection of eyes
- Contact lenses may pose a special hazard; soft contact lenses may absorb and concentrate irritants. A written policy document, describing the wearing of lens or restrictions on use, should be created for each workplace or task. This should include a review of lens absorption and adsorption for the class of chemicals in use and an account of injury experience. Medical and first-aid personnel should be trained in their removal and suitable equipment should be readily available. In the event of chemical exposure, begin eye irrigation immediately and remove contact lens as soon as practicable. Lens should be removed at the first signs of eye redness or irritation - lens should be removed in a clean environment only after workers have washed hands thoroughly. [CDC NIOSH Current Intelligence Bulletin 59].

HANDS/FEET

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

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Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

- DO NOT wear cotton or cotton-backed gloves.
- DO NOT wear leather gloves.
- Promptly hose all spills off leather shoes or boots or ensure that such footwear is protected with PVC over-shoes.

OTHER

- Overalls.
- PVC Apron.
- PVC protective suit may be required if exposure severe.
- Eyewash unit.
- Ensure there is ready access to a safety shower.
- Some plastic personal protective equipment (PPE) (e.g. gloves, aprons, overshoes) are not recommended as they may produce static electricity.
- For large scale or continuous use wear tight-weave non-static clothing (no metallic fasteners, cuffs or pockets), non sparking safety footwear.
- 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

■ 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	AX- AUS	-
1000	50	-	AX- AUS
5000	50	Airline *	-
5000	100	-	AX- 2
10000	100	-	AX- 3
	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. For further information consult site specific data (if available), or your Occupational Health and Safety Advisor.

ENGINEERING CONTROLS

■ Local exhaust ventilation usually required. If risk of overexposure exists, wear approved respirator. Correct fit is essential to obtain adequate protection. Supplied-air type respirator may be required in special circumstances. Correct fit is essential to ensure 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

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Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

air required to effectively remove the contaminant.

Type of Contaminant:

solvent, vapours, degreasing etc., evaporating from tank (in still air).

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) direct spray, spray painting in shallow booths, drum filling, conveyer loading, crusher dusts, gas discharge (active generation into zone of rapid air motion) grinding, abrasive blasting, tumbling, high speed wheel generated dusts (released at high initial velocity into zone of very high rapid air motion).

Air Speed:

0.25- 0.5 m/s (50- 100 f/min.)

0.5- 1 m/s (100- 200 f/min.)

1- 2.5 m/s (200- 500 f/min.)

2.5- 10 m/s (500- 2000 f/min.)

Within each range the appropriate value depends on:

Lower end of the range

- 1: Room air currents minimal or favourable to capture
- 2: Contaminants of low toxicity or of nuisance value only.
- 3: Intermittent, low production.
- 4: Large hood or large air mass in motion

Upper end of the range

- 1: Disturbing room air currents
- 2: Contaminants of high toxicity
- 3: High production, heavy use
- 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

APPEARANCE

Black to brownish-black fine powder with no odour. Oxidizing agent. Insoluble in water, nitric or cold sulfuric acid; slowly dissolves in cold hydrochloric acid with evolution of heat.

PHYSICAL PROPERTIES

Does not mix with water.

Sinks in water.

State	DIVIDED SOLID	Molecular Weight	86.94
Melting Range (°C)	535 (decomposes)	Viscosity	Not Applicable
Boiling Range (°C)	Not applicable.	Solubility in water (g/L)	Immiscible
Flash Point (°C)	Not applicable	pH (1% solution)	Not applicable.

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Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

Decomposition Temp (°C)	535	pH (as supplied)	Not applicable
Autoignition Temp (°C)	Not applicable	Vapour Pressure (kPa)	Not applicable.
Upper Explosive Limit (%)	Not applicable	Specific Gravity (water=1)	4.45
Lower Explosive Limit (%)	Not applicable	Relative Vapour Density (air=1)	Not applicable.
Volatile Component (%vol)	Not applicable.	Evaporation Rate	Not applicable

Section 10 - CHEMICAL STABILITY AND REACTIVITY INFORMATION

CONDITIONS CONTRIBUTING TO INSTABILITY

- Presence of incompatible materials.
 - Product is considered stable under normal handling conditions.
 - Prolonged exposure to heat.
 - Hazardous polymerisation will not occur.
- For incompatible materials - refer to Section 7 - Handling and Storage.*

Section 11 - TOXICOLOGICAL INFORMATION

POTENTIAL HEALTH EFFECTS

ACUTE HEALTH EFFECTS

SWALLOWED

- Accidental ingestion of the material may be harmful; animal experiments indicate that ingestion of less than 150 gram may be fatal or may produce serious damage to the health of the individual.
- Poisonings rarely occur after oral administration of manganese salts because they are poorly absorbed from the gut.

EYE

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

SKIN

- There is some evidence to suggest that this material can cause inflammation of the skin on contact in some persons.
- 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 dusts, generated by the material, during the course of normal handling, may be harmful.
 - 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.
- If prior damage to the circulatory or nervous systems has occurred or if kidney damage has been sustained, proper screenings should be conducted on individuals who may be exposed to further risk if handling and use of the material result in excessive exposures.
- Manganese fume is toxic and produces nervous system effects characterised by tiredness. Acute poisoning is rare although acute inflammation of the lungs may occur. A chemical pneumonia may also result from frequent exposure. Inhalation of freshly formed metal oxide particles sized below 1.5 microns and generally between 0.02 to 0.05 microns may result in "metal fume fever". Symptoms may be delayed for up to 12 hours and begin with the sudden onset of thirst, and a sweet, metallic or foul taste in the mouth. Other symptoms include upper respiratory tract irritation accompanied by coughing and a dryness of the mucous membranes, lassitude and a generalised feeling of malaise. Mild to severe headache, nausea, occasional vomiting, fever or chills,

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Section 11 - TOXICOLOGICAL INFORMATION

exaggerated mental activity, profuse sweating, diarrhoea, excessive urination and prostration may also occur. Tolerance to the fumes develops rapidly, but is quickly lost. All symptoms usually subside within 24-36 hours following removal from exposure.

■ Acute silicosis occurs under conditions of extremely high silica dust exposure particularly when the particle size of the dust is small. The disease is rapidly progressive and spreads widely through the lungs within months of the initial exposure and causing death within 1 to 2 years.

CHRONIC HEALTH EFFECTS

■ Harmful: danger of serious damage to health by prolonged exposure through inhalation.

This material can cause serious damage if one is exposed to it for long periods. It can be assumed that it contains a substance which can produce severe defects. This has been demonstrated via both short- and long-term experimentation.

Substance accumulation, in the human body, may occur and may cause some concern following repeated or long-term occupational exposure.

Long term exposure to high dust concentrations may cause changes in lung function i.e. pneumoconiosis; caused by particles less than 0.5 micron penetrating and remaining in the lung. Prime symptom is breathlessness; lung shadows show on X-ray.

Manganese is an essential trace element. Chronic exposure to low levels of manganese can include a mask-like facial expression, spastic gait, tremors, slurred speech, disordered muscle tone, fatigue, anorexia, loss of strength and energy, apathy and poor concentration.

Overexposure to respirable dust may cause coughing, wheezing, difficulty in breathing and impaired lung function. Chronic symptoms may include decreased vital lung capacity, chest infections

Repeated exposures, in an occupational setting, to high levels of fine- divided dusts may produce a condition known as pneumoconiosis which is the lodgement of any inhaled dusts in the lung irrespective of the effect.

This is particularly true when a significant number of particles less than 0.5 microns (1/50,000 inch), are present. Lung shadows are seen in the X-ray. Symptoms of pneumoconiosis may include a progressive dry cough, shortness of breath on exertion (exertional dyspnea), increased chest expansion, weakness and weight loss. As the disease progresses the cough produces a stringy mucous, vital capacity decreases further and shortness of breath becomes more severe. Other signs or symptoms include altered breath sounds, diminished lung capacity, diminished oxygen uptake during exercise, emphysema and pneumothorax (air in lung cavity) as a rare complication.

Removing workers from possibility of further exposure to dust generally leads to halting the progress of the lung abnormalities. Where worker-exposure potential is high, periodic examinations with emphasis on lung dysfunctions should be undertaken

Dust inhalation over an extended number of years may produce pneumoconiosis.. Pneumoconiosis is the accumulation of dusts in the lungs and the tissue reaction in its presence. It is further classified as being of noncollagenous or collagenous types. Noncollagenous pneumoconiosis, the benign form, is identified by minimal stromal reaction, consists mainly of reticulin fibres, an intact alveolar architecture and is potentially reversible.

TOXICITY AND IRRITATION

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

TOXICITY

Oral (Rat) LD50: >3478 mg/kg

■ No significant acute toxicological data identified in literature search.

IRRITATION

SILICA CRYSTALLINE - QUARTZ:

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

TOXICITY

Inhalation (human) LCLo: 0.3 mg/m³/10Y

Inhalation (human) TCLo: 16 mppcf*8H/17.9Y

Inhalation (rat) TCLo: 50 mg/m³/6H/71W

■ WARNING: For inhalation exposure ONLY: This substance has been classified by the IARC as Group 1: CARCINOGENIC TO HUMANS.

Intermittent; focal fibrosis,
(pneumoconiosis), cough, dyspnoea

Intermittent; liver - tumours.

IRRITATION

Nil Reported

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* Millions of particles per cubic foot (based on impinger samples counted by light field techniques).

NOTE : the physical nature of quartz in the product determines whether it is likely to present a chronic health problem. To be a hazard the material must enter the breathing zone as respirable particles.

CARCINOGEN

Silica, amorphous	International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs	Group	3
Silica, crystalline (inhaled in the form of quartz or cristobalite from occupational sources)	International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs	Group	1

Section 12 - ECOLOGICAL INFORMATION

Refer to data for ingredients, which follows:

SILICA CRYSTALLINE - QUARTZ:

MANGANESE DIOXIDE:

■ DO NOT discharge into sewer or waterways.

MANGANESE DIOXIDE:

■ For manganese and its compounds:

Environmental fate:

It has been established that while lower organisms (e.g., plankton, aquatic plants, and some fish) can significantly bioconcentrate manganese, higher organisms (including humans) tend to maintain manganese homeostasis. This indicates that the potential for biomagnification of manganese from lower trophic levels to higher ones is low.

There were two mechanisms involved in explaining the retention of manganese and other metals in the environment by soil. First, through cation exchange reactions, manganese ions and the charged surface of soil particles form manganese oxides, hydroxides, and oxyhydroxides which in turn form absorption sites for other metals. Secondly, manganese can be adsorbed to other oxides, hydroxides, and oxyhydroxides through ligand exchange reactions. When the soil solution becomes saturated, these manganese oxides, hydroxides, and oxyhydroxides can precipitate into a new mineral phase and act as a new surface to which other substances can absorb. The tendency of soluble manganese compounds to adsorb to soils and sediments depends mainly on the cation exchange capacity and the organic composition of the soil. The soil adsorption constants (the ratio of the concentration in soil to the concentration in water) for Mn(II) span five orders of magnitude, ranging from 0.2 to 10,000 mL/g, increasing as a function of the organic content and the ion exchange capacity of the soil; thus, adsorption may be highly variable. In some cases, adsorption of manganese to soils may not be a readily reversible process. At low concentrations, manganese may be "fixed" by clays and will not be released into solution readily. At higher concentrations, manganese may be desorbed by ion exchange mechanisms with other ions in solution. For example, the discharge of waste water effluent into estuarine environments resulted in the mobilization of manganese from the bottom sediments. The metals in the effluent may have been preferentially adsorbed resulting in the release of manganese. The oxidation state of manganese in soil and sediments may be altered by microbial activity; oxidation may lead to the precipitation of manganese. Bacteria and microflora can increase the mobility of manganese.

The transport and partitioning of manganese in water is controlled by the solubility of the specific chemical form present, which in turn is determined by pH, Eh (oxidation-reduction potential), and the characteristics of the available anions. The metal may exist in water in any of four oxidation states.

Manganese(II) predominates in most waters (pH 4-7) but may become oxidized at a pH >8 or 9. The principal

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anion associated with Mn(II) in water is usually carbonate (CO_3^{2-}), and the concentration of manganese is limited by the relatively low solubility (65 mg/L) of MnCO_3 . In relatively oxidized water, the solubility of Mn(II) may be controlled by manganese oxide equilibria, with manganese being converted to the Mn(II) or Mn(IV) oxidation states. In extremely reduced water, the fate of manganese tends to be controlled by formation of a poorly soluble sulfide. Manganese in water may undergo oxidation at high pH or Eh and is also subject to microbial activity. For example, Mn(II) in a lake was oxidized during the summer months, but this was inhibited by a microbial poison, indicating that the oxidation was mediated by bacteria. The microbial metabolism of manganese is presumed to be a function of pH, temperature, and other factors.

Manganese in water may be significantly bioconcentrated at lower trophic levels. A bioconcentration factor (BCF) relates the concentration of a chemical in plant and animal tissues to the concentration of the chemical in the water in which they live. The BCF of manganese was estimated as 2,500 - 6,300 for phytoplankton, 300 - 5,500 for marine algae, 80 - 830 for intertidal mussels, and 35 - 930 for coastal fish. Similarly, the BCF of manganese was estimated to be 10,000 - 20,000 for marine and freshwater plants, 10,000 - 40,000 for invertebrates, and 10 - 600 for fish. In general, these data indicate that lower organisms such as algae have larger BCFs than higher organisms. In order to protect consumers from the risk of manganese bioaccumulation in marine mollusks, the U.S. EPA has set a criterion for manganese at 0.1 mg/L for marine waters.

Elemental manganese and inorganic manganese compounds have negligible vapor pressures but may exist in air as suspended particulate matter derived from industrial emissions or the erosion of soils. Manganese-containing particles are mainly removed from the atmosphere by gravitational settling, with large particles tending to fall out faster than small particles. The half-life of airborne particles is usually on the order of days, depending on the size of the particle and atmospheric conditions. Some removal by washout mechanisms such as rain may also occur, although it is of minor significance in comparison to dry deposition.

SILICA CRYSTALLINE - QUARTZ:

■ For silica:

The literature on the fate of silica in the environment concerns dissolved silica in the aquatic environment, irrespective of its origin (man-made or natural), or structure (crystalline or amorphous). Indeed, once released and dissolved into the environment no distinction can be made between the initial forms of silica. At normal environmental pH, dissolved silica exists exclusively as monosilicic acid $[\text{Si}(\text{OH})_4]$. At pH 9.4 the solubility of amorphous silica is about 120 mg SiO_2/l . Quartz has a solubility of only 6 mg/l, but its rate of dissolution is so slow at ordinary temperature and pressure that the solubility of amorphous silica represents the upper limit of dissolved silica concentration in natural waters. Moreover, silicic acid is the bioavailable form for aquatic organisms and it plays an important role in the biogeochemical cycle of Si, particularly in the oceans.

In the oceans, the transfer of dissolved silica from the marine hydrosphere to the biosphere initiates the global biological silicon cycle. Marine organisms such as diatoms, silicoflagellates and radiolarians build up their skeletons by taking up silicic acid from seawater. After these organisms die, the biogenic silica accumulated in them partly dissolves. The portion of the biogenic silica that does not dissolve settles and ultimately reaches the sediment. The transformation of opal (amorphous biogenic silica) deposits in sediments through diagenetic processes allows silica to re-enter the geological cycle. Silica is labile between the water and sediment interface.

Ecotoxicity:

Fish LC50 (96 h): Brachydanio rerio >10000 mg/l; zebra fish >10000 mg/l

Daphnia magna EC50 (24 h): >1000 mg/l; LC50 924 h): >10000 mg/l.

■ Metal-containing inorganic substances generally have negligible vapour pressure and are not expected to partition to air. Once released to surface waters and moist soils their fate depends on solubility and dissociation in water. Environmental processes (such as oxidation and the presence of acids or bases) may transform insoluble metals to more soluble ionic forms. Microbiological processes may also transform insoluble metals to more soluble forms. Such ionic species may bind to dissolved ligands or sorb to solid particles in aquatic or aqueous media. A significant proportion of dissolved/ sorbed metals will end up in sediments through the settling of suspended particles. The remaining metal ions can then be taken up by aquatic organisms.

When released to dry soil most metals will exhibit limited mobility and remain in the upper layer; some will leach locally into ground water and/ or surface water ecosystems when soaked by rain or melt ice.

Environmental processes may also be important in changing solubilities.

Even though many metals show few toxic effects at physiological pHs, transformation may introduce new or magnified effects.

A metal ion is considered infinitely persistent because it cannot degrade further.

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The current state of science does not allow for an unambiguous interpretation of various measures of bioaccumulation.

The counter-ion may also create health and environmental concerns once isolated from the metal. Under normal physiological conditions the counter-ion may be essentially insoluble and may not be bioavailable.

Environmental processes may enhance bioavailability.

Ecotoxicity

Ingredient	Persistence: Water/Soil	Persistence: Air	Bioaccumulation	Mobility
manganese dioxide	LOW		LOW	HIGH
silica crystalline - quartz	LOW		LOW	HIGH

GESAMP/EHS COMPOSITE LIST - GESAMP Hazard Profiles

Name / Cas No / RTECS No	EHS	TRN	A1a	A1b	A1	A2	B1	B2	C1	C2	C3	D1	D2	D3	E1	E2	E3
-	151	250	Ino	0	0	Ino	0	0	(0)	(0)	NI	(0)	(0)			S	0
CAS:1313- 13- 9 /	4	7	rg			rg											

Legend:

EHS=EHS Number (EHS=GESAMP Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships) NRT=Net Register Tonnage, A1a=Bioaccumulation log Pow, A1b=Bioaccumulation BCF, A1=Bioaccumulation, A2=Biodegradation, B1=Acute aquatic toxicity LC/EC50 (mg/l), B2=Chronic aquatic toxicity NOEC (mg/l), C1=Acute mammalian oral toxicity LD50 (mg/kg), C2=Acute mammalian dermal toxicity LD50 (mg/kg), C3=Acute mammalian inhalation toxicity LC50 (mg/kg), D1=Skin irritation & corrosion, D2=Eye irritation & corrosion, D3=Long-term health effects, E1=Tainting, E2=Physical effects on wildlife & benthic habitats, E3=Interference with coastal amenities,

For column A2: R=Readily biodegradable, NR=Not readily biodegradable.

For column D3: C=Carcinogen, M=Mutagenic, R=Reprotoxic, S=Sensitising, A=Aspiration hazard, T=Target organ systemic toxicity, L=Lung injury, N=Neurotoxic, I=Immunotoxic.

For column E1: NT=Not tainting (tested), T=Tainting test positive.

For column E2: Fp=Persistent floater, F=Floater, S=Sinking substances.

The numerical scales start from 0 (no hazard), while higher numbers reflect increasing hazard.

(GESAMP/EHS Composite List of Hazard Profiles - Hazard evaluation of substances transported by ships)

Section 13 - DISPOSAL CONSIDERATIONS

- Containers may still present a chemical hazard/ danger when empty.
- Return to supplier for reuse/ recycling if possible.

Otherwise:

- If container can not be cleaned sufficiently well to ensure that residuals do not remain or if the container cannot be used to store the same product, then puncture containers, to prevent re-use, and bury at an authorised landfill.

- Where possible retain label warnings and MSDS and observe all notices pertaining to the product.

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

continued...

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Section 13 - DISPOSAL CONSIDERATIONS

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 or process equipment to enter drains.
- It may be necessary to collect all wash water for treatment before disposal.
- In all cases disposal to sewer may be subject to local laws and regulations and these should be considered first.
- Where in doubt contact the responsible authority.
- Recycle wherever possible or consult manufacturer for recycling options.
- Consult State Land Waste Management Authority for disposal.
- Bury residue in an authorised landfill.
- Recycle containers if possible, or dispose of in an authorised landfill.

Section 14 - TRANSPORTATION INFORMATION



Labels Required: OXIDIZING AGENT

HAZCHEM:

☐ 1Y

Land Transport UNDG:

Class or division:	5.1	Subsidiary risk:	None
UN No.:	1479	UN packing group:	II
Shipping Name: OXIDIZING SOLID, N.O.S. (contains manganese dioxide)			

Air Transport IATA:

ICAO/IATA Class:	5.1	ICAO/IATA Subrisk:	None
UN/ID Number:	1479	Packing Group:	II
Special provisions:	A3		
Shipping Name: OXIDIZING SOLID, N.O.S. *(CONTAINS MANGANESE DIOXIDE)			

Maritime Transport IMDG:

IMDG Class:	5.1	IMDG Subrisk:	None
UN Number:	1479	Packing Group:	II
EMS Number:	F- A, S- Q	Special provisions:	223 274 900 944
Limited Quantities:	5 kg		
Shipping Name: OXIDIZING SOLID, N.O.S.(contains manganese dioxide)			

GESAMP hazard profiles for this material can be found in section 12 of the MSDS.

Section 15 - REGULATORY INFORMATION

REGULATIONS

manganese dioxide (CAS: 1313-13-9) is found on the following regulatory lists;

"Australia Hazardous Substances", "Australia Inventory of Chemical Substances (AICS)", "Australia Therapeutic Goods Administration (TGA) Substances that may be

continued...

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Section 15 - REGULATORY INFORMATION

used as active ingredients in Listed medicines", "OECD Representative List of High Production Volume (HPV) Chemicals"
Regulations for ingredients

silica crystalline - quartz (CAS: 14808-60-7, 122304-48-7, 122304-49-8, 12425-26-2, 1317-79-9, 70594-95-5, 87347-84-0) is found on the following regulatory lists;

"Australia - New South Wales Hazardous Substances Prohibited for Specific Uses", "Australia - New South Wales Hazardous Substances Requiring Health Surveillance", "Australia - South Australia Hazardous Substances Requiring Health Surveillance", "Australia - Tasmania Hazardous Substances Prohibited for Specified Uses", "Australia - Tasmania Hazardous Substances Requiring Health Surveillance", "Australia - Western Australia Hazardous Substances Requiring Health Surveillance", "Australia Exposure Standards", "Australia Hazardous Substances", "Australia Hazardous Substances Requiring Health Surveillance", "Australia High Volume Industrial Chemical List (HVICL)", "Australia Inventory of Chemical Substances (AICS)", "Australia Occupational Health and Safety (Commonwealth Employment) (National Standards) Regulations 1994 - Hazardous Substances Requiring Health Surveillance", "International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs", "OECD Representative List of High Production Volume (HPV) Chemicals"

Section 16 - OTHER INFORMATION

INGREDIENTS WITH MULTIPLE CAS NUMBERS

Ingredient Name	CAS
silica crystalline - quartz	14808- 60- 7, 122304- 48- 7, 122304- 49- 8, 12425- 26- 2, 1317- 79- 9, 70594- 95- 5, 87347- 84- 0

MSDS SECTION CHANGES

The following table displays the version number of and date on which each section was last changed.

Section Name	Version	Date	Section Name	Version	Date	Section Name	Version	Date
Advice to Doctor	4	23- Jun- 2005	Storage (storage incompatibility)	4	23- Jun- 2005	Acute Health (eye)	4	23- Jun- 2005
First Aid (inhaled)	4	23- Jun- 2005	Storage (storage requirement)	4	23- Jun- 2005	Acute Health (inhaled)	4	23- Jun- 2005
First Aid (skin)	4	23- Jun- 2005	Storage (suitable container)	4	23- Jun- 2005	Acute Health (skin)	4	23- Jun- 2005
First Aid (swallowed)	4	23- Jun- 2005	Engineering Control	4	23- Jun- 2005	Acute Health (swallowed)	4	23- Jun- 2005
Fire Fighter (extinguishing media)	4	23- Jun- 2005	Personal Protection (eye)	4	23- Jun- 2005	Chronic Health	4	23- Jun- 2005
Fire Fighter (fire fighting)	4	23- Jun- 2005	Personal Protection (hands/feet)	4	23- Jun- 2005	Toxicity and Irritation (Toxicity Figure)	4	23- Jun- 2005
Fire Fighter (fire incompatibility)	4	23- Jun- 2005	Personal Protection (other)	4	23- Jun- 2005	Environmental	4	23- Jun- 2005
Fire Fighter (fire/explosion hazard)	4	23- Jun- 2005	Appearance	6	22- Feb- 2008	Disposal	4	23- Jun- 2005
Spills (major)	4	23- Jun- 2005	Instability Condition	4	23- Jun- 2005			

■ Classification of the preparation and its individual components has drawn on official and authoritative sources as well as independent review by using available literature 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.

The above information is believed to be accurate and represent the best information currently available to us, but does not represent any warranty expressed or implied of the properties of the product. User should make their own investigation to determine the suitability of the information for their particular purpose.

Issue Date: 22-Feb-2018