

## SAFETY DATA SHEET

### WANNATE PM-200

WANHUA CHEMICAL GROUP Co., LTD.

Version No: 27.25

Safety Data Sheet Safety Data Sheet - Authored according to GB/T16483(2008) and GB/T17519(2013)

Chemwatch Hazard Alert Code: 2

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## SECTION 1 IDENTIFICATION OF THE SUBSTANCE / MIXTURE AND OF THE COMPANY / UNDERTAKING

### Product Identifier

Product name	WANNATE PM-200
Synonyms	Polymethylene polyphenylene isocyanate
Other means of identification	Not Available

### Relevant identified uses of the substance or mixture and uses advised against

Relevant identified uses	Polyurethane material, PU foam raw material.
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### Details of the supplier of the safety data sheet

Registered company name	WANHUA CHEMICAL GROUP Co., LTD.
Address	No.17 Tianshan Road, Yantai, Shandong China
Telephone	0535-3031150
Fax	0535-338222-1150
Website	http://www.whchem.com
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### Emergency telephone number

Association / Organisation	Emergency Center of China
Emergency telephone numbers	+86 532-83889090
Other emergency telephone numbers	+86 535-8203123

## SECTION 2 HAZARDS IDENTIFICATION


### Classification of the substance or mixture

#### SUMMARY OF HAZARD IN AN EMERGENCY SITUATION

Liquid.Combustible.  
Harmful by inhalation.  
Irritating to eyes.  
Irritating to respiratory system.  
Irritating to skin.  
May cause SENSITISATION by inhalation.  
May cause SENSITISATION by skin contact.  
Danger of cumulative effects.  
Limited evidence of a carcinogenic effect.  
Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.

Classification [1]	Eye Irritation Category 2A, Respiratory Sensitizer Category 1, Specific target organ toxicity - repeated exposure Category 2, Acute Toxicity (Inhalation) Category 4, Specific target organ toxicity - single exposure Category 3 (respiratory tract irritation), Skin Corrosion/Irritation Category 2, Skin Sensitizer Category 1, Carcinogenicity Category 2
Legend:	1. Classified by Chemwatch; 2. China Classification Information Sheet of Hazardous Chemicals (Draft); 3. Classification drawn from Regulation (EU) No 1272/2008 - Annex VI

### Label elements

Hazard pictogram(s)	
SIGNAL WORD	DANGER

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## Hazard statement(s)

H319	Causes serious eye irritation.
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H373	May cause damage to organs through prolonged or repeated exposure. (Respiratory system) (Dermal)
H332	Harmful if inhaled.
H335	May cause respiratory irritation.
H315	Causes skin irritation.
H317	May cause an allergic skin reaction.
H351	Suspected of causing cancer.

## Precautionary statement(s) Prevention

P201	Obtain special instructions before use.
P260	Do not breathe mist/vapours/spray.
P271	Use only outdoors or in a well-ventilated area.
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P284	[In case of inadequate ventilation] wear respiratory protection.
P261	Avoid breathing mist/vapours/spray.
P202	Do not handle until all safety precautions have been read and understood.
P264	Wash all exposed external body areas thoroughly after handling.
P272	Contaminated work clothing should not be allowed out of the workplace.

## Precautionary statement(s) Response

P308+P313	IF exposed or concerned: Get medical advice/ attention.
P321	Specific treatment (see advice on this label).
P342+P311	If experiencing respiratory symptoms: Call a POISON CENTER/doctor/physician/first aider.
P305+P351+P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P312	Call a POISON CENTER/doctor/physician/first aider/if you feel unwell.
P314	Get medical advice/attention if you feel unwell.
P333+P313	If skin irritation or rash occurs: Get medical advice/attention.
P337+P313	If eye irritation persists: Get medical advice/attention.
P302+P352	IF ON SKIN: Wash with plenty of water.
P304+P340	IF INHALED: Remove person to fresh air and keep comfortable for breathing.
P332+P313	If skin irritation occurs: Get medical advice/attention.
P362+P364	Take off contaminated clothing and wash it before reuse.

## Precautionary statement(s) Storage

P405	Store locked up.
P403+P233	Store in a well-ventilated place. Keep container tightly closed.

## Precautionary statement(s) Disposal

P501	Dispose of contents/container to authorised hazardous or special waste collection point in accordance with any local regulation.
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## Physical and Chemical Hazard

Liquid. Combustible.  
Vapours/gas heavier than air.  
Toxic smoke/fumes in a fire.  
Reacts with water.

## Health Hazards

Inhaled	<p>Evidence shows, or practical experience predicts, that the material produces irritation of the respiratory system, in a substantial number of individuals, following inhalation. In contrast to most organs, the lung is able to respond to a chemical insult by first removing or neutralising the irritant and then repairing the damage. The repair process, which initially evolved to protect mammalian lungs from foreign matter and antigens, may however, produce further lung damage resulting in the impairment of gas exchange, the primary function of the lungs. Respiratory tract irritation often results in an inflammatory response involving the recruitment and activation of many cell types, mainly derived from the vascular system.</p> <p>The material has <b>NOT</b> been classified by EC Directives or other classification systems as 'harmful by inhalation'. This is because of the lack of corroborating animal or human evidence. In the absence of such evidence, care should be taken nevertheless to ensure exposure is kept to a minimum and that suitable control measures be used, in an occupational setting to control vapours, fumes and aerosols.</p> <p>The vapour/mist may be highly irritating to the upper respiratory tract and lungs; the response may be severe enough to produce bronchitis and pulmonary oedema. Possible neurological symptoms arising from isocyanate exposure include headache, insomnia, euphoria, ataxia, anxiety neurosis, depression and paranoia. Gastrointestinal disturbances are characterised by nausea and vomiting. Pulmonary sensitisation may produce asthmatic reactions ranging from minor breathing difficulties to severe allergic attacks; this may occur following a single acute exposure or may develop without warning for several hours after exposure. Sensitized people can react to very low doses, and should not be allowed to work in situations allowing exposure to this material. Continued exposure of sensitised persons may lead to possible long term respiratory impairment.</p>
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	Inhalation hazard is increased at higher temperatures.
<b>Ingestion</b>	The material has <b>NOT</b> been classified by EC Directives or other classification systems as 'harmful by ingestion'. This is because of the lack of corroborating animal or human evidence. The material may still be damaging to the health of the individual, following ingestion, especially where pre-existing organ (e.g liver, kidney) damage is evident. Present definitions of harmful or toxic substances are generally based on doses producing mortality rather than those producing morbidity (disease, ill-health). Gastrointestinal tract discomfort may produce nausea and vomiting. In an occupational setting however, ingestion of insignificant quantities is not thought to be cause for concern.
<b>Skin Contact</b>	<p>Evidence exists, or practical experience predicts, that the material either produces inflammation of the skin in a substantial number of individuals following direct contact, and/or produces significant inflammation when applied to the healthy intact skin of animals, for up to four hours, such inflammation being present twenty-four hours or more after the end of the exposure period. Skin irritation may also be present after prolonged or repeated exposure; this may result in a form of contact dermatitis (nonallergic). The dermatitis is often characterised by skin redness (erythema) and swelling (oedema) which may progress to blistering (vesiculation), scaling and thickening of the epidermis. At the microscopic level there may be intercellular oedema of the spongy layer of the skin (spongiosis) and intracellular oedema of the epidermis.</p> <p>The material may accentuate any pre-existing dermatitis condition</p> <p>Skin contact is not thought to have harmful health effects (as classified under EC Directives); the material may still produce health damage following entry through wounds, lesions or abrasions.</p> <p>Open cuts, abraded or irritated skin should not be exposed to this material</p> <p>Entry into the blood-stream through, for example, cuts, abrasions, puncture wounds 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.</p>
<b>Eye</b>	Evidence exists, or practical experience predicts, that the material may cause eye irritation in a substantial number of individuals and/or may produce significant ocular lesions which are present twenty-four hours or more after instillation into the eye(s) of experimental animals. Repeated or prolonged eye contact may cause inflammation characterised by a temporary redness (similar to windburn) of the conjunctiva (conjunctivitis); temporary impairment of vision and/or other transient eye damage/ulceration may occur.
<b>Chronic</b>	<p>On the basis, primarily, of animal experiments, concern has been expressed that the material may produce carcinogenic or mutagenic effects; in respect of the available information, however, there presently exists inadequate data for making a satisfactory assessment.</p> <p>Repeated or long-term occupational exposure is likely to produce cumulative health effects involving organs or biochemical systems.</p> <p>Long-term exposure to respiratory irritants may result in disease of the airways involving difficult breathing and related systemic problems.</p> <p>Practical evidence shows that inhalation of the material is capable of inducing a sensitisation reaction in a substantial number of individuals at a greater frequency than would be expected from the response of a normal population.</p> <p>Pulmonary sensitisation, resulting in hyperactive airway dysfunction and pulmonary allergy may be accompanied by fatigue, malaise and aching.</p> <p>Significant symptoms of exposure may persist for extended periods, even after exposure ceases. Symptoms can be activated by a variety of nonspecific environmental stimuli such as automobile exhaust, perfumes and passive smoking.</p> <p>Practical experience shows that skin contact with the material is capable either of inducing a sensitisation reaction in a substantial number of individuals, and/or of producing a positive response in experimental animals.</p> <p>Persons with a history of asthma or other respiratory problems or are known to be sensitised, should not be engaged in any work involving the handling of isocyanates.</p> <p>The chemistry of reaction of isocyanates, as evidenced by MDI, in biological milieu is such that in the event of a true exposure of small MDI doses to the mouth, reactions will commence at once with biological macromolecules in the buccal region and will continue along the digestive tract prior to reaching the stomach. Reaction products will be a variety of polyureas and macromolecular conjugates with for example mucus, proteins and cell components.</p> <p>This is corroborated by the results from an MDI inhalation study. Following an inhalation exposure of rats to radiolabelled MDI, 79% of the dose was excreted in faeces. The faecal excretion in these animals was considered entirely due to ingestion of radioactivity from grooming and ingestion of deposited material from the nasopharyngeal region via the mucociliary escalator, i.e. not following systemic absorption. The faecal radioactivity was tentatively identified as mixed molecular weight polyureas derived from MDI. Diamine was not present. Thus, for MDI and diisocyanates in general the oral gavage dosing route is inappropriate for toxicological studies and risk assessment.</p> <p>It is expected that oral gavage dosing will result in a similar outcome to that produced by TDI or MDI, that is (1) reaction with stomach contents and (2) polymerization to solid polyureas.</p> <ul style="list-style-type: none"> <li>Reaction with stomach contents is very plausibly described in case reports of accidental ingestion of polymeric MDI based glue in domestic animals. Extensive polymerization and CO<sub>2</sub> liberation resulting in an expansion of the gastric content is described in the stomach, without apparent acute chemical toxicity</li> <li>Polyurea formation in organic and aqueous phases has been described. In this generally accepted chemistry of hydrolysis of an isocyanate the initially produced carbamate decarboxylates to an amine which. The amine, as a reactive intermediate, then reacts very readily with the present isocyanate to produce a solid and inert polyurea. This urea formation acts as a pH buffer in the stomach, thus promoting transformation of the diisocyanate into polyurea, even under the acidic conditions.</li> </ul> <p>At the absorptive tissues in the small intestine, these high molecular reaction products are likely to be of very low bioavailability, which is substantiated by the absence of systemic toxicity in acute oral bioassays with rats at the OECD limit dose (LC50&gt;2 g/kg bw).</p> <p>The respiratory tract may be regarded as the main entry for systemically available isocyanates as evidenced following MDI exposures. A detailed summary on urinary, plasma and in vitro metabolite studies is provided below. Taken together, all available studies provide convincing evidence that MDI-protein adduct and MDI-metabolite formation proceeds:</p> <ul style="list-style-type: none"> <li>via formation of a labile isocyanate glutathione (GSH)-adduct,</li> <li>then transfer to a more stable adduct with larger proteins, and</li> <li>without formation of free MDA. MDA reported as a metabolite is actually formed by analytical workup procedures (strong acid or base hydrolysis) and is not an identified metabolite in urine or blood</li> </ul> <p>Isocyanate vapours/mists are irritating to the upper respiratory tract and lungs; the response may be severe enough to produce bronchitis with wheezing, gasping and severe distress, even sudden loss of consciousness, and pulmonary oedema. Possible neurological symptoms arising from isocyanate exposure include headache, insomnia, euphoria, ataxia, anxiety neurosis, depression and paranoia. Gastrointestinal disturbances are characterised by nausea and vomiting. Pulmonary sensitisation may produce asthmatic reactions ranging from minor breathing difficulties to severe allergic attacks; this may occur following a single acute exposure or may develop without warning after a period of tolerance. A respiratory response may occur following minor skin contact. Skin sensitisation is possible and may result in allergic dermatitis responses including rash, itching, hives and swelling of extremities.</p> <p>Isocyanate-containing vapours/ mists may cause inflammation of eyes and nasal passages.</p> <p>Onset of symptoms may be immediate or delayed for several hours after exposure. Sensitised people can react to very low levels of airborne isocyanates. Unprotected or sensitised persons should not be allowed to work in situations allowing exposure to this material.</p>

**Environmental Hazards**

See Section 12

**Other hazards****SECTION 3 COMPOSITION / INFORMATION ON INGREDIENTS**

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**Substances**

See section below for composition of Mixtures

**Mixtures**

CAS No	%[weight]	Name
9016-87-9*	>=99	polymeric diphenylmethane diisocyanate
		Note: CAS 101-68-8 is an MDI isomer and part of CAS 9016-87-9.

**SECTION 4 FIRST AID MEASURES****Description of first aid measures**

<b>Eye Contact</b>	<p>If this product comes in contact with the eyes:</p> <ul style="list-style-type: none"> <li>Wash out immediately with fresh running water.</li> <li>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.</li> <li>Seek medical attention without delay; if pain persists or recurs seek medical attention.</li> <li>Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.</li> </ul>
<b>Skin Contact</b>	<p>If skin contact occurs:</p> <ul style="list-style-type: none"> <li>Immediately remove all contaminated clothing, including footwear.</li> <li>Flush skin and hair with running water (and soap if available).</li> <li>Seek medical attention in event of irritation.</li> </ul>
<b>Inhalation</b>	<ul style="list-style-type: none"> <li>If fumes or combustion products are inhaled remove from contaminated area.</li> <li>Lay patient down. Keep warm and rested.</li> <li>Prostheses such as false teeth, which may block airway, should be removed, where possible, prior to initiating first aid procedures.</li> <li>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.</li> <li>Transport to hospital, or doctor, without delay.</li> </ul> <p>Following uptake by inhalation, move person to an area free from risk of further exposure. Oxygen or artificial respiration should be administered as needed. Asthmatic-type symptoms may develop and may be immediate or delayed up to several hours. Treatment is essentially symptomatic. A physician should be consulted.</p>
<b>Ingestion</b>	<ul style="list-style-type: none"> <li>Immediately give a glass of water.</li> <li>First aid is not generally required. If in doubt, contact a Poisons Information Centre or a doctor.</li> </ul>

**Advise for rescue team (PPE requirement for rescue personnel)****Indication of any immediate medical attention and special treatment needed**

For sub-chronic and chronic exposures to isocyanates:

- This material may be a potent pulmonary sensitiser which causes bronchospasm even in patients without prior airway hyperreactivity.
- Clinical symptoms of exposure involve mucosal irritation of respiratory and gastrointestinal tracts.
- Conjunctival irritation, skin inflammation (erythema, pain vesiculation) and gastrointestinal disturbances occur soon after exposure.
- Pulmonary symptoms include cough, burning, substernal pain and dyspnoea.
- Some cross-sensitivity occurs between different isocyanates.
- Noncardiogenic pulmonary oedema and bronchospasm are the most serious consequences of exposure. Markedly symptomatic patients should receive oxygen, ventilatory support and an intravenous line.
- Treatment for asthma includes inhaled sympathomimetics (epinephrine [adrenalin], terbutaline) and steroids.
- Activated charcoal (1 g/kg) and a cathartic (sorbitol, magnesium citrate) may be useful for ingestion.
- Mydriatics, systemic analgesics and topical antibiotics (Sulamyd) may be used for corneal abrasions.
- There is no effective therapy for sensitised workers.

[Ellenhorn and Barceloux; Medical Toxicology]

**NOTE:** Isocyanates cause airway restriction in naive individuals with the degree of response dependant on the concentration and duration of exposure. They induce smooth muscle contraction which leads to bronchoconstrictive episodes. Acute changes in lung function, such as decreased FEV1, may not represent sensitivity.

[Karol & Jin, Frontiers in Molecular Toxicology, pp 56-61, 1992]

Personnel who work with isocyanates, isocyanate prepolymers or polyisocyanates should have a pre-placement medical examination and periodic examinations thereafter, including a pulmonary function test. Anyone with a medical history of chronic respiratory disease, asthmatic or bronchial attacks, indications of allergic responses, recurrent eczema or sensitisation conditions of the skin should not handle or work with isocyanates. Anyone who develops chronic respiratory distress when working with isocyanates should be removed from exposure and examined by a physician. Further exposure must be avoided if a sensitivity to isocyanates or polyisocyanates has developed.

**SECTION 5 FIREFIGHTING MEASURES****Extinguishing media**

- Small quantities of water in contact with hot liquid may react violently with generation of a large volume of rapidly expanding hot sticky semi-solid foam.
- Presents additional hazard when fire fighting in a confined space.
- Cooling with flooding quantities of water reduces this risk.
- Water spray or fog may cause frothing and should be used in large quantities.
- Foam.
- Dry chemical powder.
- BCF (where regulations permit).
- Carbon dioxide.
- Water spray or fog - Large fires only.

**Special hazards arising from the substrate or mixture**

<b>Fire Incompatibility</b>	Avoid contamination with oxidising agents i.e. nitrates, oxidising acids, chlorine bleaches, pool chlorine etc. as ignition may result
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## Advice for firefighters

Fire Fighting	<ul style="list-style-type: none"> <li>▶ Alert Fire Brigade and tell them location and nature of hazard.</li> <li>▶ Wear full body protective clothing with breathing apparatus.</li> <li>▶ Prevent, by any means available, spillage from entering drains or water course.</li> <li>▶ Use water delivered as a fine spray to control fire and cool adjacent area.</li> <li>▶ Avoid spraying water onto liquid pools.</li> <li>▶ <b>DO NOT</b> approach containers suspected to be hot.</li> <li>▶ Cool fire exposed containers with water spray from a protected location.</li> <li>▶ If safe to do so, remove containers from path of fire.</li> </ul>
Fire/Explosion Hazard	<ul style="list-style-type: none"> <li>- Combustible.</li> <li>- Moderate fire hazard when exposed to heat or flame.</li> <li>- When heated to high temperatures decomposes rapidly generating vapour which pressurises and may then rupture containers with release of flammable and highly toxic isocyanate vapour.</li> <li>- Burns with acrid black smoke and poisonous fumes.</li> <li>- Due to reaction with water producing CO<sub>2</sub>-gas, a hazardous build-up of pressure could result if contaminated containers are re-sealed.</li> <li>- Combustion yields traces of highly toxic hydrogen cyanide HCN, plus toxic nitrogen oxides NO<sub>x</sub> and carbon monoxide.</li> </ul> <p>Combustion products include: carbon dioxide (CO<sub>2</sub>) hydrogen cyanide isocyanates and minor amounts of nitrogen oxides (NO<sub>x</sub>) other pyrolysis products typical of burning organic material. May emit corrosive fumes.</p> <p>When heated at high temperatures many isocyanates decompose rapidly generating a vapour which pressurises containers, possibly to the point of rupture. Release of toxic and/or flammable isocyanate vapours may then occur</p>

## SECTION 6 ACCIDENTAL RELEASE MEASURES

## Personal precautions, protective equipment and emergency procedures

See section 8

## Measures for Preventing Secondary Contamination

Refer to section above

## Environmental precautions

See section 12

## Methods and material for containment and cleaning up

Minor Spills	<ul style="list-style-type: none"><li>▶ Remove all ignition sources.</li><li>▶ Clean up all spills immediately.</li><li>▶ Avoid breathing vapours and contact with skin and eyes.</li><li>▶ Control personal contact with the substance, by using protective equipment.</li><li>▶ Contain and absorb spill with sand, earth, inert material or vermiculite.</li><li>▶ Wipe up.</li><li>▶ Place in a suitable, labelled container for waste disposal.</li></ul>																																																																	
Major Spills	<p>Chemical Class: cyanates and isocyanates</p> <p>For release onto land: recommended sorbents listed in order of priority.</p> <table><tr><th>SORBENT TYPE</th><th>RANK</th><th>APPLICATION</th><th>COLLECTION</th><th>LIMITATIONS</th></tr></table> <p>LAND SPILL - SMALL</p> <table><tr><td>cross-linked polymer - particulate</td><td>1</td><td>shovel</td><td>shovel</td><td>R,W,SS</td></tr><tr><td>wood fiber - particulate</td><td>1</td><td>throw</td><td>pitchfork</td><td>R, P, DGC, RT</td></tr><tr><td>cross-linked polymer - pillow</td><td>1</td><td>throw</td><td>pitchfork</td><td>R, DGC, RT</td></tr><tr><td>sorbent clay - particulate</td><td>2</td><td>shovel</td><td>shovel</td><td>R, I, P</td></tr><tr><td>foamed glass - pillow</td><td>2</td><td>throw</td><td>pitchfork</td><td>R, P, DGC, RT</td></tr><tr><td>wood fiber - particulate</td><td>3</td><td>shovel</td><td>shovel</td><td>R, W, P, DGC</td></tr></table> <p>LAND SPILL - MEDIUM</p> <table><tr><td>cross-linked polymer -particulate</td><td>1</td><td>blower</td><td>skiploader</td><td>R, W, SS</td></tr><tr><td>cross-linked polymer - pillow</td><td>1</td><td>throw</td><td>skiploader</td><td>R,DGC, RT</td></tr><tr><td>polypropylene - particulate</td><td>2</td><td>blower</td><td>skiploader</td><td>R, SS, DGC</td></tr><tr><td>expanded mineral - particulate</td><td>3</td><td>blower</td><td>skiploader</td><td>R, I, W, P, DGC</td></tr><tr><td>wood fiber - particulate</td><td>3</td><td>blower</td><td>skiploader</td><td>R, W, P, DGC</td></tr><tr><td>polypropylene - mat</td><td>3</td><td>throw</td><td>skiploader</td><td>DGC, RT</td></tr></table> <p>Legend</p> <p>DGC: Not effective where ground cover is dense</p> <p>R; Not reusable</p> <p>I: Not incinerable</p>	SORBENT TYPE	RANK	APPLICATION	COLLECTION	LIMITATIONS	cross-linked polymer - particulate	1	shovel	shovel	R,W,SS	wood fiber - particulate	1	throw	pitchfork	R, P, DGC, RT	cross-linked polymer - pillow	1	throw	pitchfork	R, DGC, RT	sorbent clay - particulate	2	shovel	shovel	R, I, P	foamed glass - pillow	2	throw	pitchfork	R, P, DGC, RT	wood fiber - particulate	3	shovel	shovel	R, W, P, DGC	cross-linked polymer -particulate	1	blower	skiploader	R, W, SS	cross-linked polymer - pillow	1	throw	skiploader	R,DGC, RT	polypropylene - particulate	2	blower	skiploader	R, SS, DGC	expanded mineral - particulate	3	blower	skiploader	R, I, W, P, DGC	wood fiber - particulate	3	blower	skiploader	R, W, P, DGC	polypropylene - mat	3	throw	skiploader	DGC, RT
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## WANNATE PM-200

- P: Effectiveness reduced when rainy  
 RT: Not effective where terrain is rugged  
 SS: Not for use within environmentally sensitive sites  
 W: Effectiveness reduced when windy  
 Reference: Sorbents for Liquid Hazardous Substance Cleanup and Control;  
 R.W Melvold et al: Pollution Technology Review No. 150: Noyes Data Corporation 1988
- ▶ Liquid Isocyanates and high isocyanate vapour concentrations will penetrate seals on self contained breathing apparatus - SCBA should be used inside encapsulating suit where this exposure may occur.
- For isocyanate spills of less than 40 litres (2 m<sup>2</sup>):
- ▶ Evacuate area from everybody not dealing with the emergency, keep them upwind and prevent further access, remove ignition sources and, if inside building, ventilate area as well as possible.
  - ▶ Notify supervision and others as necessary.
  - ▶ Put on personal protective equipment (suitable respiratory protection, face and eye protection, protective suit, gloves and impermeable boots).
  - ▶ Control source of leakage (where applicable).
  - ▶ Dike the spill to prevent spreading and to contain additions of decontaminating solution.
  - ▶ Prevent the material from entering drains.
  - ▶ Estimate spill pool volume or area.
  - ▶ Absorb and decontaminate. - Completely cover the spill with wet sand, wet earth, vermiculite or other similar absorbent. - Add neutraliser (for suitable formulations: see below) to the adsorbent materials (equal to that of estimated spill pool volume). Intensify contact between spill, absorbent and neutraliser by carefully mixing with a rake and allow to react for 15 minutes
  - ▶ Shovel absorbent/decontaminant solution mixture into a steel drum.
  - ▶ Decontaminate surface. - Pour an equal amount of neutraliser solution over contaminated surface. - Scrub area with a stiff bristle brush, using moderate pressure. - Completely cover decontaminant with vermiculite or other similar absorbent. - After 5 minutes, shovel absorbent/decontamination solution mixture into the same steel drum used above.
  - ▶ Monitor for residual isocyanate. If surface is decontaminated, proceed to next step. If contamination persists, repeat decontaminate procedure immediately above
  - ▶ Place loosely covered drum (release of carbon dioxide) outside for at least 72 hours. Label waste-containing drum appropriately. Remove waste materials for incineration.
  - ▶ Decontaminate and remove personal protective equipment.
  - ▶ Return to normal operation.
  - ▶ Conduct accident investigation and consider measures to prevent reoccurrence.

**Decontamination:**

Treat isocyanate spills with sufficient amounts of isocyanate decontaminant preparation ('neutralising fluid'). Isocyanates and polyisocyanates are generally not miscible with water. Liquid surfactants are necessary to allow better dispersion of isocyanate and neutralising fluids/ preparations. Alkaline neutralisers react faster than water/surfactant mixtures alone.

Typically, such a preparation may consist of:

Sawdust: 20 parts by weight Kieselguhr 40 parts by weight plus a mixture of {ammonia (s.g. 0.880) 8% v/v non-ionic surfactant 2% v/v water 90% v/v}.

Let stand for 24 hours

Three commonly used neutralising fluids each exhibit advantages in different situations.

**Formulation A :**

liquid surfactant	0.2-2%
sodium carbonate	5-10%
water to	100%

**Formulation B**

liquid surfactant	0.2-2%
concentrated ammonia	3-8%
water to	100%

**Formulation C**

ethanol, isopropanol or butanol	50%
concentrated ammonia	5%
water to	100%

After application of any of these formulae, let stand for 24 hours.

Formulation B reacts faster than Formulation A. However, ammonia-based neutralisers should be used only under well-ventilated conditions to avoid overexposure to ammonia or if members of the emergency team wear suitable respiratory protection. Formulation C is especially suitable for cleaning of equipment from unreacted isocyanate and neutralizing under freezing conditions. Regard has to be taken to the flammability of the alcoholic solution.

- ▶ Avoid contamination with water, alkalies and detergent solutions.
- ▶ Material reacts with water and generates gas, pressurises containers with even drum rupture resulting.
- ▶ **DO NOT reseal container if contamination is suspected.**
- ▶ Open all containers with care.

Moderate hazard.

- ▶ Clear area of personnel and move upwind.
- ▶ Alert Fire Brigade and tell them location and nature of hazard.
- ▶ Wear breathing apparatus plus protective gloves.
- ▶ Prevent, by any means available, spillage from entering drains or water course.
- ▶ No smoking, naked lights or ignition sources.
- ▶ Increase ventilation.
- ▶ Stop leak if safe to do so.
- ▶ Contain spill with sand, earth or vermiculite.
- ▶ Collect recoverable product into labelled containers for recycling.
- ▶ Absorb remaining product with sand, earth or vermiculite.
- ▶ Collect solid residues and seal in labelled drums for disposal.
- ▶ Wash area and prevent runoff into drains.
- ▶ If contamination of drains or waterways occurs, advise emergency services.

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

**SECTION 7 HANDLING AND STORAGE****Precautions for safe handling**

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Safe handling	<ul style="list-style-type: none"> <li>▶ Avoid all personal contact, including inhalation.</li> <li>▶ Wear protective clothing when risk of exposure occurs.</li> <li>▶ Use in a well-ventilated area.</li> <li>▶ Prevent concentration in hollows and sumps.</li> <li>▶ <b>DO NOT enter confined spaces until atmosphere has been checked.</b></li> <li>▶ Avoid smoking, naked lights or ignition sources.</li> <li>▶ Avoid contact with incompatible materials.</li> <li>▶ When handling, <b>DO NOT eat, drink or smoke.</b></li> <li>▶ Keep containers securely sealed when not in use.</li> <li>▶ Avoid physical damage to containers.</li> <li>▶ Always wash hands with soap and water after handling.</li> <li>▶ Work clothes should be laundered separately.</li> <li>▶ Use good occupational work practice.</li> <li>▶ Observe manufacturer's storage and handling recommendations contained within this SDS.</li> <li>▶ Atmosphere should be regularly checked against established exposure standards to ensure safe working conditions.</li> <li>▶ <b>DO NOT allow clothing wet with material to stay in contact with skin</b></li> </ul>
Other information	<p>for commercial quantities of isocyanates:</p> <ul style="list-style-type: none"> <li>▶ Isocyanates should be stored in adequately bunded areas. Nothing else should be kept within the same bunding. Pre-polymers need not be segregated. Drums of isocyanates should be stored under cover, out of direct sunlight, protected from rain, protected from physical damage and well away from moisture, acids and alkalis.</li> <li>▶ Where isocyanates are stored at elevated temperatures to prevent solidifying, adequate controls should be installed to prevent the high temperatures and precautions against fire should be taken.</li> <li>▶ Where stored in tanks, the more reactive isocyanates should be blanketed with a non-reactive gas such as nitrogen and equipped with absorptive type breather valve (to prevent vapour emissions)..</li> <li>▶ Transfer systems for isocyanates in bulk storage should be fully enclosed and use pump or vacuum systems. Warning signs, in appropriate languages, should be posted where necessary.</li> <li>▶ Areas in which polyurethane foam products are stored should be supplied with good general ventilation. Residual amounts of unreacted isocyanate may be present in the finished foam, resulting in hazardous atmospheric concentrations.</li> </ul> <ul style="list-style-type: none"> <li>▶ Store in original containers.</li> <li>▶ Keep containers securely sealed.</li> <li>▶ No smoking, naked lights or ignition sources.</li> <li>▶ Store in a cool, dry, well-ventilated area.</li> <li>▶ Store away from incompatible materials and foodstuff containers.</li> <li>▶ Protect containers against physical damage and check regularly for leaks.</li> <li>▶ Observe manufacturer's storage and handling recommendations contained within this SDS.</li> </ul>

## Conditions for safe storage, including any incompatibilities

Suitable container	<ul style="list-style-type: none"> <li>▶ Metal can or drum</li> <li>▶ Packaging as recommended by manufacturer.</li> <li>▶ Check all containers are clearly labelled and free from leaks.</li> </ul>
Storage incompatibility	<ul style="list-style-type: none"> <li>▶ Avoid cross contamination between the two liquid parts of product (kit).</li> <li>▶ If two part products are mixed or allowed to mix in proportions other than manufacturer's recommendation, polymerisation with gelation and evolution of heat (exotherm) may occur.</li> <li>▶ This excess heat may generate toxic vapour</li> <li>· Avoid reaction with water, alcohols and detergent solutions. Isocyanates are electrophiles, and as such they are reactive toward a variety of nucleophiles including alcohols, amines, and even water. Upon treatment with an alcohol, an isocyanate forms a urethane linkage. If a di-isocyanate is treated with a compound containing two or more hydroxyl groups, such as a diol or a polyol, polymer chains are formed, which are known as polyurethanes. Reaction between a di-isocyanate and a compound containing two or more amine groups, produces long polymer chains known as polyureas.</li> <li>· Isocyanates and thioisocyanates are incompatible with many classes of compounds, reacting exothermically to release toxic gases. Reactions with amines, strong bases, aldehydes, alcohols, alkali metals, ketones, mercaptans, strong oxidisers, hydrides, phenols, and peroxides can cause vigorous releases of heat. Acids and bases initiate polymerisation reactions in these materials.</li> <li>· Isocyanates also can react with themselves. Aliphatic di-isocyanates can form trimers, which are structurally related to cyanuric acid. Isocyanates participate in Diels-Alder reactions, functioning as dienophiles</li> <li>· Isocyanates easily form adducts with carbodiimides, isothiocyanates, ketenes, or with substrates containing activated CC or CN bonds.</li> <li>· Some isocyanates react with water to form amines and liberate carbon dioxide. This reaction may also generate large volumes of foam and heat. Foaming spaces may produce pressure in confined spaces or containers. Gas generation may pressurise drums to the point of rupture.</li> <li>· Do NOT reseal container if contamination is expected</li> <li>· Open all containers with care</li> <li>· Base-catalysed reactions of isocyanates with alcohols should be carried out in inert solvents. Such reactions in the absence of solvents often occur with explosive violence,</li> <li>· Isocyanates will attack and embrittle some plastics and rubbers.</li> <li>· The isocyanate anion is a pseudohalide (syn pseudohalogen) whose chemistry, resembling that of the true halogens, allows it to substitute for halogens in several classes of chemical compounds.. The behavior and chemical properties of the several pseudohalides are identical to that of the true halide ions.</li> </ul> <p>▶ A range of exothermic decomposition energies for isocyanates is given as 20-30 kJ/mol.</p> <p>▶ The relationship between energy of decomposition and processing hazards has been the subject of discussion; it is suggested that values of energy released per unit of mass, rather than on a molar basis (J/g) be used in the assessment.</p> <p>▶ For example, in 'open vessel processes' (with man-hole size openings, in an industrial setting), substances with exothermic decomposition energies below 500 J/g are unlikely to present a danger, whilst those in 'closed vessel processes' (opening is a safety valve or bursting disk) present some danger where the decomposition energy exceeds 150 J/g.</p> <p>BREITHERICK: Handbook of Reactive Chemical Hazards, 4th Edition</p>

## SECTION 8 EXPOSURE CONTROLS / PERSONAL PROTECTION

## Control parameters

| OCCUPATIONAL EXPOSURE LIMITS (OEL)

| INGREDIENT DATA



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Source	Ingredient	Material name	TWA	STEL	Peak	Notes
China Occupational Exposure Limits for Hazardous Agents in the Workplace	4,4'-diphenylmethane diisocyanate (MDI)	二苯基甲烷二异氰酸酯	0.05 mg/m3	0.1 mg/m3	Not Available	敏

## EMERGENCY LIMITS

Ingredient	Material name	TEEL-1	TEEL-2	TEEL-3
polymeric diphenylmethane diisocyanate	Polymethylene polyphenyl isocyanate; (Polymeric diphenylmethane diisocyanate)	0.15 mg/m3	3.6 mg/m3	22 mg/m3
4,4'-diphenylmethane diisocyanate (MDI)	Methylene diphenyl diisocyanate; (Diphenylmethane diisocyanate; MDI)	0.45 mg/m3	Not Available	Not Available
4,4'-diphenylmethane diisocyanate (MDI)	Methylenebis(isocyanato-benzene), 1,1'-; (Diphenyl methane diisocyanate)	29 mg/m3	40 mg/m3	240 mg/m3

Ingredient	Original IDLH	Revised IDLH
polymeric diphenylmethane diisocyanate	Not Available	Not Available
4,4'-diphenylmethane diisocyanate (MDI)	75 mg/m3	Not Available

## OCCUPATIONAL EXPOSURE BANDING

Ingredient	Occupational Exposure Band Rating	Occupational Exposure Band Limit
polymeric diphenylmethane diisocyanate	E	≤ 0.1 ppm

## Notes:

Occupational exposure banding is a process of assigning chemicals into specific categories or bands based on a chemical's potency and the adverse health outcomes associated with exposure. The output of this process is an occupational exposure band (OEB), which corresponds to a range of exposure concentrations that are expected to protect worker health.

## MATERIAL DATA



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for isocyanates:

Some jurisdictions require that health surveillance be conducted on occupationally exposed workers. This should emphasise:

- ▶ demography, occupational and medical history and health advice
- ▶ completion of a standardised respiratory questionnaire
- ▶ physical examination of the respiratory system and skin
- ▶ standardised respiratory function tests such as FEV1, FVC and FEV1/FVC

Various portable or stationary instruments are available for the continuous measurement of isocyanates in the air. All of them function on the principle of colourimetric evaluation of an indicator paper strip. They are operating continuously and unattended. Paper tape systems are easy to use and do not require skilled analysts to operate them. They give rapid results and are therefore suitable for leak detection and in emergency situations. However,:

- ▶ they may read incorrect at very high or very low humidity,
- ▶ are unsuitable for aerosols
- ▶ and may not be accepted for purposes of regulatory compliance.

Air monitoring of isocyanates requires sound analytical knowledge. In order to obtain reliable results only laboratories with experience in that specific area should be engaged with such measurements

In the evaluation of the German MAK Commission the justification of the OEL for 4,4'-MDI/ pMDI is established based on the isocyanate (NCO) group which is common to the monomeric, oligomeric and the polymeric MDIs. This NCO group is highly reactive (see toxicokinetics and category justification for details). Due to this high reactivity of the functional NCO group towards nucleophilic biomolecules the primary health effect of MDI is irritation at the point of contact, which can be demonstrated by the numerous acute, subacute and chronic bioassays, and sensitization.

The most sensitive health effect resulting from acute inhalation exposure to respirable aerosols of MDI is irritation to predominately the bronchio-alveolar part of the respiratory tract. After inhalation exposure, MDI reacts with nucleophilic low and higher-molecular components of the liquid films that cover the airways, glutathione (GSH) represents the most important nucleophile in quantitative terms. The low-molecular adducts or conjugates of MDI are absorbed and direct transcarbamoylation results in plasma protein adducts (albumin, haemoglobin). All observed health effects resulting from exposure to respirable aerosols in acute, subchronic or chronic bioassays and human studies can be allocated to primary alveolar reactivity (respiratory irritation and/or sensitization). No systemic effect other than secondary to primary irritation has been described.

Biomonitoring for exposure to diisocyanates typically looks to assay derivatives (diamines) following hydrolysis of biological fluids and is routinely employed to measure occupational exposure to MDI and other diisocyanates. For diamine analysis, samples of urine are typically used, although blood samples can also be used. However, these markers are not specific for the diisocyanate exposure. The urine biomarkers (after acid or base hydrolysis) reflected recent exposures whereas certain haemoglobin (Hb) biomarkers did not necessarily correlate with the urine biomarkers, and were considered to reflect overall exposures over a longer term. The hydrolysis methods and conditions used release differing amounts of the diamine analyte.

Hydrolysis analytes are at low concentrations and proportionally little of the dose is in urine or blood, and that there is no standardised method for measuring biomarkers in hydrolyzed urine. Investigation of diisocyanate specific biomarkers has focused on the conjugated molecules in blood. Typically, conjugates with Hb or albumin (Alb) have been assessed, and there has been progress in application of experiments in animals to biomonitoring of human exposures to MDI.

The role for glutathione as an intermediary in transport of diisocyanates is now supported by good evidence using various model compounds. The most probable reactions of isocyanates with biological macromolecules are with the amine (mixed urea), the hydroxyl (carbamate) and the sulphhydryl (thiolytic acid ester) and that latter is of a reversible nature. The thiocarbamate bond of isocyanate-sulphydryl is reversible, and various authors have found release and transfer of MDI moieties from thiocarbamate conjugates to other nucleophiles, notably protein. The conjugates were shown to be recognised by serum IgG from MDI exposed workers, demonstrating a non-enzymatic, thiol-mediated transcarbamoylating mechanism to protein.

The methods to identify and quantify MDI-adducts to plasma proteins particularly albumin (Alb) and to haemoglobin (Hb) have now been applied to biological monitoring, particularly useful since the amount of adducts would be indicative of an integrated exposure. In addition these adducts are specific for MDI exposure. However the total amount of the analyte MDA, retrievable from Hb-adducts and urinary precursors, accounts for less than 0.5 % of the applied dose of MDI, and the lack of linearity of biomarker to exposure dose makes uncertain the extrapolation from the yield of biomarkers in urine or blood towards inhalative MDI exposure. The use of protein adducts for biomonitoring appears to overcome some of these difficulties and benefits from specificity of the analyte. To date no diisocyanate specific urinary biomarker has been identified. For blood, the MDI-specific methods developed are: Hb-conjugate derived hydantoin, Alb-lysine conjugates and peptide conjugates. On the basis of limits of detection, the Hb-hydantoin method is most sensitive compared to the Alb-lysine method which in turn is more sensitive than the signature peptide method. The Hb-hydantoin method covers a longer period of exposure than the Alb-lysine, due to the longer half life of the erythrocyte compared to serum albumin.

for diphenylmethane diisocyanate (methylene bisphenyl isocyanate; MDI)

Odour Threshold Value: 0.39 ppm

IDLH Level: 10 mg/m<sup>3</sup>

Mean MDI exposures of less than 0.003 ppm appear to have no acute or chronic effect on pulmonary function.

MDI produces identical toxicological responses to those produced by TDI and the recommended TLV-TWA is identical for the two isocyanates. Exposure at or below the recommended value is thought to protect the worker against pulmonary function decrements as well as to minimise the potential for respiratory tract sensitisation. Individuals who may be hypersusceptible or otherwise unusually responsive to exposure to certain industrial chemicals may not adequately protected from adverse health effects caused by MDI at the recommended TLV-TWA. Ceiling values recommended by NIOSH and OSHA are synonymous with normal excursions allowable for exposures to the TLV-TWA (in excess of 3 x TLV-TWA for no more than a total of 30 minutes during a work day but in any case not exceeding 5 x TLV-TWA).

## Exposure controls

### Appropriate engineering controls

Engineering controls are used to remove a hazard or place a barrier between the worker and the hazard. Well-designed engineering controls can be highly effective in protecting workers and will typically be independent of worker interactions to provide this high level of protection.

The basic types of engineering controls are:

Process controls which involve changing the way a job activity or process is done to reduce the risk.

Enclosure and/or isolation of emission source which keeps a selected hazard 'physically' away from the worker and ventilation that strategically 'adds' and 'removes' air in the work environment. Ventilation can remove or dilute an air contaminant if designed properly. The design of a ventilation system must match the particular process and chemical or contaminant in use.

Employers may need to use multiple types of controls to prevent employee overexposure.

- ▶ Spraying of material or material in admixture with other components must be carried out in conditions conforming to local state regulations (AS/NZS 4114, UNI EN 12215:2010, ANSI/IIHA Z9.3-2007 or national equivalent).
- ▶ Local exhaust ventilation with full face positive-pressure air supplied breathing apparatus (hood or helmet type) is required.
- ▶ Spraying should be performed in a spray booth fitted with an effective exhaust system which complies with local environmental legislation.
- ▶ The spray booth area must be isolated from unprotected personnel whilst spraying is in progress and until all spraying mist has cleared.


**NOTE:** Isocyanate vapours will not be adequately absorbed by organic vapour respirators. Air contaminants generated in the workplace possess varying 'escape' velocities which, in turn, determine the 'capture velocities' of fresh circulating air required to effectively remove the contaminant.

Type of Contaminant:	Air Speed:
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.)

Within each range the appropriate value depends on:

Lower end of the range	Upper end of the range
1: Room air currents minimal or favourable 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

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	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 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 solvents generated by spraying at a point 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.
<b>Personal protection</b>	
<b>Eye and face protection</b>	<ul style="list-style-type: none"> <li>▶ Safety glasses with side shields.</li> <li>▶ Chemical goggles.</li> <li>▶ Contact lenses may pose a special hazard; soft contact lenses may absorb and concentrate irritants. A written policy document, describing the wearing of lenses 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], [AS/NZS 1336 or national equivalent]</li> </ul>
<b>Skin protection</b>	See Hand protection below
<b>Hands/feet protection</b>	<p><b>NOTE:</b></p> <ul style="list-style-type: none"> <li>▶ The material may produce skin sensitisation in predisposed individuals. Care must be taken, when removing gloves and other protective equipment, to avoid all possible skin contact.</li> <li>▶ Contaminated leather items, such as shoes, belts and watch-bands should be removed and destroyed.</li> </ul> <p>The selection of suitable gloves does not only depend on the material, but also on further marks of quality which vary from manufacturer to manufacturer. Where the chemical is a preparation of several substances, the resistance of the glove material can not be calculated in advance and has therefore to be checked prior to the application.</p> <p>The exact break through time for substances has to be obtained from the manufacturer of the protective gloves and has to be observed when making a final choice.</p> <p>Personal hygiene is a key element of effective hand care. 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.</p> <p>Suitability and durability of glove type is dependent on usage. Important factors in the selection of gloves include:</p> <ul style="list-style-type: none"> <li>- frequency and duration of contact,</li> <li>- chemical resistance of glove material,</li> <li>- glove thickness and</li> <li>- dexterity</li> </ul> <p>Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739, AS/NZS 2161.1 or national equivalent).</p> <ul style="list-style-type: none"> <li>- 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, AS/NZS 2161.10.1 or national equivalent) is recommended.</li> <li>- 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, AS/NZS 2161.10.1 or national equivalent) is recommended.</li> <li>- Some glove polymer types are less affected by movement and this should be taken into account when considering gloves for long-term use.</li> <li>- Contaminated gloves should be replaced.</li> </ul> <p>As defined in ASTM F-739-96 in any application, gloves are rated as:</p> <ul style="list-style-type: none"> <li>- Excellent when breakthrough time &gt; 480 min</li> <li>- Good when breakthrough time &gt; 20 min</li> <li>- Fair when breakthrough time &lt; 20 min</li> <li>- Poor when glove material degrades</li> </ul> <p>For general applications, gloves with a thickness typically greater than 0.35 mm, are recommended.</p> <p>It should be emphasised that glove thickness is not necessarily a good predictor of glove resistance to a specific chemical, as the permeation efficiency of the glove will be dependent on the exact composition of the glove material. Therefore, glove selection should also be based on consideration of the task requirements and knowledge of breakthrough times.</p> <p>Glove thickness may also vary depending on the glove manufacturer, the glove type and the glove model. Therefore, the manufacturers' technical data should always be taken into account to ensure selection of the most appropriate glove for the task.</p> <p>Note: Depending on the activity being conducted, gloves of varying thickness may be required for specific tasks. For example:</p> <ul style="list-style-type: none"> <li>- Thinner gloves (down to 0.1 mm or less) may be required where a high degree of manual dexterity is needed. However, these gloves are only likely to give short duration protection and would normally be just for single use applications, then disposed of.</li> <li>- Thicker gloves (up to 3 mm or more) may be required where there is a mechanical (as well as a chemical) risk i.e. where there is abrasion or puncture potential</li> </ul> <p>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.</p> <ul style="list-style-type: none"> <li>▶ Isocyanate resistant materials include Teflon, Viton, nitrile rubber and some PVA gloves.</li> <li>▶ Protective gloves and overalls should be worn as specified in the appropriate national standard.</li> <li>▶ Contaminated garments should be removed promptly and should not be re-used until they have been decontaminated.</li> <li>▶ NOTE: Natural rubber, neoprene, PVC can be affected by isocyanates</li> </ul>
<b>Body protection</b>	See Other protection below
<b>Other protection</b>	<ul style="list-style-type: none"> <li>▶ Overalls.</li> <li>▶ P.V.C. apron.</li> <li>▶ Barrier cream.</li> <li>▶ Skin cleansing cream.</li> <li>▶ Eye wash unit.</li> </ul>

**Recommended material(s)****GLOVE SELECTION INDEX**

Glove selection is based on a modified presentation of the:

**'Forsberg Clothing Performance Index'.**

The effect(s) of the following substance(s) are taken into account in the **computer-generated** selection:

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**Respiratory protection****Full face respirator with supplied air.**

- ▶ Cartridge respirators should never be used for emergency ingress or in areas of unknown vapour concentrations or oxygen content.
- ▶ The wearer must be warned to leave the contaminated area immediately on detecting any odours through the respirator. The odour may indicate that the

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Material	CPI
PE/EVAL/PE	A

\* CPI - Chemwatch Performance Index

A: Best Selection

B: Satisfactory; may degrade after 4 hours continuous immersion

C: Poor to Dangerous Choice for other than short term immersion

**NOTE:** As a series of factors will influence the actual performance of the glove, a final selection must be based on detailed observation. -

\* Where the glove is to be used on a short term, casual or infrequent basis, factors such as 'feel' or convenience (e.g. disposability), may dictate a choice of gloves which might otherwise be unsuitable following long-term or frequent use. A qualified practitioner should be consulted.

mask is not functioning properly, that the vapour concentration is too high, or that the mask is not properly fitted. Because of these limitations, only restricted use of cartridge respirators is considered appropriate.

- ▶ Cartridge performance is affected by humidity. Cartridges should be changed after 2 hr of continuous use unless it is determined that the humidity is less than 75%, in which case, cartridges can be used for 4 hr. Used cartridges should be discarded daily, regardless of the length of time used
- ▶ In certain circumstances, personal protection of the individual employee is necessary. Personal protective devices should be regarded as being supplementary to substitution and engineering control and should not be used in preference to them as they do nothing to eliminate the hazard.
- ▶ However, in some situations, minimising exposure to isocyanates by enclosure and ventilation is not possible, and occupational exposure standards may be exceeded, particularly during on-site mixing of paints, spray-painting, foaming and maintenance of machine and ventilation systems. In these situations, air-line respirators or self-contained breathing apparatus complying with the appropriate national standard must be used.
- ▶ Organic vapour respirators with particulate pre- filters and powered, air-purifying respirators are NOT suitable.
- ▶ Personal protective equipment must be appropriately selected, individually fitted and workers trained in their correct use and maintenance. Personal protective equipment must be regularly checked and maintained to ensure that the worker is being protected.
- ▶ Air- line respirators or self-contained breathing apparatus complying with the appropriate national standard should be used during the clean-up of spills and the repair or clean-up of contaminated equipment and similar situations which cause emergency exposures to hazardous atmospheric concentrations of isocyanate.

## SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

## Information on basic physical and chemical properties

Appearance	Brown		
Physical state	Liquid	Relative density (Water = 1)	1.22-1.25
Odour	Not Available	Partition coefficient n-octanol / water	Not Available
Odour threshold	Not Available	Auto-ignition temperature (°C)	>600
pH (as supplied)	Not Available	Decomposition temperature	Not Available
Melting point / freezing point (°C)	Not Available	Viscosity (cSt)	Not Available
Initial boiling point and boiling range (°C)	>204	Molecular weight (g/mol)	Not Available
Flash point (°C)	>230	Taste	Not Available
Evaporation rate	Not Available	Explosive properties	Not Available
Flammability	Not Applicable	Oxidising properties	Not Available
Upper Explosive Limit (%)	Not Available	Surface Tension (dyn/cm or mN/m)	Not Available
Lower Explosive Limit (%)	Not Available	Volatile Component (%vol)	Not Available
Vapour pressure (kPa)	Not Available	Gas group	Not Available
Solubility in water	Partly miscible	pH as a solution (1%)	Not Available
Vapour density (Air = 1)	3.24	VOC g/L	Not Available

## SECTION 10 STABILITY AND REACTIVITY

Reactivity	See section 7
Chemical stability	<ul style="list-style-type: none"> <li>▶ Unstable in the presence of incompatible materials.</li> <li>▶ Product is considered stable.</li> <li>▶ Hazardous polymerisation will not occur.</li> <li>▶ Presence of elevated temperatures.</li> </ul>
Possibility of hazardous reactions	See section 7
Conditions to avoid	See section 7
Incompatible materials	See section 7
Hazardous decomposition products	See section 5

## SECTION 11 TOXICOLOGICAL INFORMATION

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	Not Available	Not Available
polymeric diphenylmethane diisocyanate		
	TOXICITY	IRRITATION
	Dermal (rabbit) LD50: >9400 mg/kg <sup>[2]</sup>	Eye (rabbit): 100 mg - mild
	Inhalation (rat) LC50: 367.95-558.98 mg/m3Air/4h <sup>[1]</sup>	Inhalation: adverse effect observed ( irritating)[1]
	Oral (rat) LD50: 2000 mg/kg <sup>[2]</sup>	Skin: adverse effect observed (irritating) <sup>[1]</sup>
4,4'-diphenylmethane diisocyanate (MDI)		
	TOXICITY	IRRITATION
	Dermal (rabbit) LD50: >6200 mg/kg <sup>[2]</sup>	Dermal Sensitiser *
	Oral (rat) LD50: >2000 mg/kg <sup>[1]</sup>	Inhalation: adverse effect observed ( irritating)[1]
	Inhalation (rat) LC50: 367.95-558.98 mg/m3Air/4h <sup>[1]</sup>	Skin (rabbit): 500 mg /24 hours
	Repeated exposure (inhalation): Adverse effects were observed in LOAEC1 mg/m3 (long-term, rats).	Skin: adverse effect observed (irritating) <sup>[1]</sup>
Legend:	1. Value obtained from Europe ECHA Registered Substances - Acute toxicity 2.* Value obtained from manufacturer's SDS. Unless otherwise specified data extracted from RTECS - Register of Toxic Effect of chemical Substances	

polymeric diphenylmethane diisocyanate	product
4,4'-DIPHENYLMETHANE DIISOCYANATE (MDI)	Inhalation (human) TClO: 0.13 ppm/30 mins Eye (rabbit): 0.10 mg moderate
WANNATE PM-200 & polymeric diphenylmethane diisocyanate & 4,4'-DIPHENYLMETHANE DIISOCYANATE (MDI)	<p>Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a non-allergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound. Key criteria for the diagnosis of RADS include the absence of preceding respiratory disease, in a non-atopic individual, with abrupt onset of persistent asthma-like symptoms within minutes to hours of a documented exposure to the irritant. A reversible airflow pattern, on spirometry, with the presence of moderate to severe bronchial hyperreactivity on methacholine challenge testing and the lack of minimal lymphocytic inflammation, without eosinophilia, have also been included in the criteria for diagnosis of RADS. RADS (or asthma) following an irritating inhalation is an infrequent disorder with rates related to the concentration of and duration of exposure to the irritating substance. Industrial bronchitis, on the other hand, is a disorder that occurs as result of exposure due to high concentrations of irritating substance (often particulate in nature) and is completely reversible after exposure ceases. The disorder is characterised by dyspnea, cough and mucus production.</p> <p>Allergic reactions which develop in the respiratory passages as bronchial asthma or rhinoconjunctivitis, are mostly the result of reactions of the allergen with specific antibodies of the IgE class and belong in their reaction rates to the manifestation of the immediate type. In addition to the allergen-specific potential for causing respiratory sensitisation, the amount of the allergen, the exposure period and the genetically determined disposition of the exposed person are likely to be decisive. Factors which increase the sensitivity of the mucosa may play a role in predisposing a person to allergy. They may be genetically determined or acquired, for example, during infections or exposure to irritant substances. Immunologically the low molecular weight substances become complete allergens in the organism either by binding to peptides or proteins (haptens) or after metabolism (prohaptens).</p> <p>Particular attention is drawn to so-called atopic diathesis which is characterised by an increased susceptibility to allergic rhinitis, allergic bronchial asthma and atopic eczema (neurodermatitis) which is associated with increased IgE synthesis.</p> <p>Exogenous allergic alveolitis is induced essentially by allergen specific immune-complexes of the IgG type; cell-mediated reactions (T lymphocytes) may be involved. Such allergy is of the delayed type with onset up to four hours following exposure.</p> <p>The following information refers to contact allergens as a group and may not be specific to this product.</p> <p>Contact allergies quickly manifest themselves as contact eczema, more rarely as urticaria or Quincke's oedema. 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 sensitisation potential: the distribution of the substance and the opportunities for contact with it are equally important. A weakly sensitising substance which is widely distributed can be a more important allergen than one with stronger sensitising 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>
polymeric diphenylmethane diisocyanate & 4,4'-DIPHENYLMETHANE DIISOCYANATE (MDI)	<p>Isocyanate vapours/mists are irritating to the upper respiratory tract and lungs; the response may be severe enough to produce bronchitis with wheezing, gasping and severe distress, even sudden loss of consciousness, and pulmonary oedema. Possible neurological symptoms arising from isocyanate exposure include headache, insomnia, euphoria, ataxia, anxiety neurosis, depression and paranoia. Gastrointestinal disturbances are characterised by nausea and vomiting. Pulmonary sensitisation may produce asthmatic reactions ranging from minor breathing difficulties to severe allergic attacks; this may occur following a single acute exposure or may develop without warning after a period of tolerance. A respiratory response may occur following minor skin contact. Skin sensitisation is possible and may result in allergic dermatitis responses including rash, itching, hives and swelling of extremities.</p> <p>Isocyanate-containing vapours/ mists may cause inflammation of eyes and nasal passages.</p> <p>Onset of symptoms may be immediate or delayed for several hours after exposure. Sensitised people can react to very low levels of airborne isocyanates. Unprotected or sensitised persons should not be allowed to work in situations allowing exposure to this material.</p> <p>The material may produce moderate eye irritation leading to inflammation. Repeated or prolonged exposure to irritants may produce conjunctivitis.</p> <p>for diisocyanates:</p> <p>In general, there appears to be little or no difference between aromatic and aliphatic diisocyanates as toxicants. In addition, there are insufficient data available to make any major distinctions between polymeric (&lt;1000 MW) and monomeric diisocyanates. Based on repeated dose studies in animals by the inhalation route, both aromatic and aliphatic diisocyanates appear to be of high concern for pulmonary toxicity at low exposure levels. Based upon a very limited data set, it appears that diisocyanate prepolymers exhibit the same respiratory tract effects as the monomers in repeated dose studies. There is also evidence that both aromatic and aliphatic diisocyanates are acutely toxic via the inhalation route. Most members of the diisocyanate category have not been tested for carcinogenic potential. Though the aromatic diisocyanates tested positive and the one aliphatic diisocyanate tested negative in one species, it is premature to make any generalizations about the carcinogenic potential of aromatic versus aliphatic diisocyanates. In the absence of more human data, it would be prudent at this time to assume that both aromatic and aliphatic diisocyanates are respiratory sensitisers. Diisocyanates are moderate to strong dermal sensitisers in animal studies. Skin irritation studies performed on rabbits and guinea pigs indicate no difference in the effects of aromatic versus aliphatic diisocyanates.</p> <p>For monomers, effects on the respiratory tract (lungs and nasal cavities) were observed in animal studies at exposure concentrations of less than 0.005 mg/L. The experimental animal data available on prepolymeric diisocyanates show similar adverse effects at levels that range from 0.002 mg/L to 0.026 mg/L.</p> <p>There is also evidence that both aromatic and aliphatic diisocyanates are acutely toxic via the inhalation route</p> <p><b>Oncogenicity:</b> Most members of the diisocyanate category have not been tested for carcinogenic potential. Commercially available Poly-MDI</p>

## WANNATE PM-200

was tested in a 2-year inhalation study in rats. The tested material contained 47% aromatic 4,4'-methylenediphenyl diisocyanate (MDI) and 53% higher molecular weight oligomers. Interim sacrifices at one year showed that males and females in the highest dose group (6 mg/m<sup>3</sup>) had treatment related histological changes in the nasal cavity, lungs and mediastinal lymph nodes. The incidence and severity of degeneration and basal cell hyperplasia of the olfactory epithelium and Bowman's gland hyperplasia were increased in males at the mid and high doses and in females at the high dose following the two year exposure period. Pulmonary adenomas were found in 6 males and 2 females, and pulmonary adenocarcinoma in one male in the high dose group. However, aliphatic hexamethylene diisocyanate (HDI) was found not to be carcinogenic in a two year repeated dose study in rats by the inhalation route. HDI has not been tested in mice by the inhalation route.

Though the oral route is not an expected route of exposure to humans, it should be noted that in two year repeated dose studies by the oral route, aromatic toluene diisocyanate (TDI) and 3,3'-dimethoxy-benzidine-4,4'-diisocyanate (dianisidine diisocyanate, DADI) were found to be carcinogenic in rodents. TDI induced a statistically significant increase in the incidence of liver tumors in rats and mice as well as dose-related hemangiosarcomas of the circulatory system and has been classified by the Agency as a B2 carcinogen. DADI was found to be carcinogenic in rats, but not in mice, with a statistically increase in the incidence of pancreatic tumors observed.

**Respiratory and Dermal Sensitization:** Based on the available toxicity data in animals and epidemiologic studies of humans, aromatic diisocyanates such as TDI and MDI are strong respiratory sensitizers. Aliphatic diisocyanates are generally not active in animal models for respiratory sensitization. However, HDI and possibly isophorone diisocyanate (IPDI), are reported to be associated with respiratory sensitization in humans. Symptoms resulting from occupational exposure to HDI include shortness of breath, increased bronchoconstriction reaction to histamine challenges, asthmatic reactions, wheezing and coughing. Two case reports of human exposure to IPDI by inhalation suggest IPDI is a respiratory sensitizer in humans. In view of the information from case reports in humans, it would be prudent at this time to assume that both aromatic and aliphatic diisocyanates are respiratory sensitizers. Studies in both human and mice using TDI, HDI, MDI and dicyclohexylmethane-4,4'-diisocyanate (HMDI) suggest cross-reactivity with the other diisocyanates, irrespective of whether the challenge compound was an aliphatic or aromatic diisocyanate. Diisocyanates are moderate to strong dermal sensitizers in animal studies. There seems to be little or no difference in the level of reactivity between aromatic and aliphatic diisocyanates.

**Dermal Irritation:** Skin irritation studies performed on rabbits and guinea pigs indicate no difference in the effects of aromatic versus aliphatic diisocyanates. The level of irritation ranged from slightly to severely irritating to the skin. One chemical, hydrogenated MDI (1,1-methylenebis-4-isocyanatocyclohexane), was found to be corrosive to the skin in guinea pigs.

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.

Acute Toxicity	✓	Carcinogenicity	✓
Skin Irritation/Corrosion	✓	Reproductivity	✗
Serious Eye Damage/Irritation	✓	STOT - Single Exposure	✓
Respiratory or Skin sensitisation	✓	STOT - Repeated Exposure	✓
Mutagenicity	✗	Aspiration Hazard	✗

**Legend:** ✗ – Data either not available or does not fill the criteria for classification  
 ✓ – Data available to make classification

## SECTION 12 ECOLOGICAL INFORMATION

## Toxicity

WANNATE PM-200	ENDPOINT	TEST DURATION (HR)	SPECIES	VALUE	SOURCE
	Not Available	Not Available	Not Available	Not Available	Not Available
polymeric diphenylmethane diisocyanate	ENDPOINT	TEST DURATION (HR)	SPECIES	VALUE	SOURCE
	LC50	4 days	Fish (acute)	>1 g/L	2
	EC50	72	Algae or other aquatic plants	>1.64 g/L	2
4,4'-diphenylmethane diisocyanate (MDI)	ENDPOINT	TEST DURATION (HR)	SPECIES	VALUE	SOURCE
	LC50	4 days	Fish (acute)	1 g/L	6
	EC50	24 h	Fresh water invertebrates	129.7-1000 g/L	2
	EC50	24h	Algae	1.64 g/L	2
<b>Legend:</b>	Extracted from 1. IUCLID Toxicity Data 2. Europe ECHA Registered Substances - Ecotoxicological Information - Aquatic Toxicity 3. EPIWIN Suite V3.12 (QSAR) - Aquatic Toxicity Data (Estimated) 4. US EPA, Ecotox database - Aquatic Toxicity Data 5. ECETOC Aquatic Hazard Assessment Data 6. NITE (Japan) - Bioconcentration Data 7. METI (Japan) - Bioconcentration Data 8. Vendor Data				

**DO NOT** discharge into sewer or waterways.

## Persistence and degradability

Ingredient	Persistence: Water (25°C)	Persistence: Air
4,4'-diphenylmethane diisocyanate (MDI)	LOW (Half-life = 20 hours)	LOW (Half-life = 1 day)

## Bioaccumulative potential

Ingredient	Bioaccumulation
4,4'-diphenylmethane diisocyanate (MDI)	LOW (BCF = 200)

## Mobility in soil

Ingredient	Mobility
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## WANNATE PM-200

4,4'-diphenylmethane diisocyanate (MDI)

LOW (KOC = 376200)

## Other adverse effects

No data available

## SECTION 13 DISPOSAL CONSIDERATIONS

## Waste treatment methods

Waste chemicals:	<ul style="list-style-type: none"> <li>Containers may still present a chemical hazard/ danger when empty.</li> <li>Return to supplier for reuse/ recycling if possible.</li> </ul> <p>Otherwise:</p> <ul style="list-style-type: none"> <li>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.</li> <li>Where possible retain label warnings and SDS and observe all notices pertaining to the product.</li> </ul> <p>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.</p> <p>A Hierarchy of Controls seems to be common - the user should investigate:</p> <ul style="list-style-type: none"> <li>Reduction</li> <li>Reuse</li> <li>Recycling</li> <li>Disposal (if all else fails)</li> </ul> <p>This material may be recycled if unused, or if it has not been contaminated so as to make it unsuitable for its intended use. If it has been contaminated, it may be possible to reclaim the product by filtration, distillation or some other means. Shelf life considerations should also be applied in making decisions of this type. Note that properties of a material may change in use, and recycling or reuse may not always be appropriate.</p> <ul style="list-style-type: none"> <li><b>DO NOT allow wash water from cleaning or process equipment to enter drains.</b></li> <li>It may be necessary to collect all wash water for treatment before disposal.</li> <li>In all cases disposal to sewer may be subject to local laws and regulations and these should be considered first.</li> <li>Where in doubt contact the responsible authority.</li> <li><b>DO NOT recycle spilled material.</b></li> <li>Consult State Land Waste Management Authority for disposal.</li> <li>Neutralise spill material carefully and decontaminate empty containers and spill residues with 10% ammonia solution plus detergent or a proprietary decontaminant prior to disposal.</li> <li><b>DO NOT seal or stopper drums being decontaminated as CO2 gas is generated and may pressurise containers.</b></li> <li>Puncture containers to prevent re-use.</li> <li>Bury or incinerate residues at an approved site.</li> </ul>
Contaminated packing materials:	Refer to section above
Precautions for Transport:	Refer to section above

## SECTION 14 TRANSPORT INFORMATION

## Labels Required

Marine Pollutant	NO
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Land transport (UN): NOT REGULATED FOR TRANSPORT OF DANGEROUS GOODS

Air transport (ICAO-IATA / DGR): NOT REGULATED FOR TRANSPORT OF DANGEROUS GOODS

Sea transport (IMDG-Code / GGVSee): NOT REGULATED FOR TRANSPORT OF DANGEROUS GOODS

Transport in bulk according to Annex II of MARPOL and the IBC code

Not Applicable

## Precautions for Transport

## Suitable Containers

See section 7

## SECTION 15 REGULATORY INFORMATION

## Safety, health and environmental regulations / legislation specific for the substance or mixture

## POLYMERIC DIPHENYLMETHANE DIISOCYANATE IS FOUND ON THE FOLLOWING REGULATORY LISTS

China Inventory of Existing Chemical Substances	International Agency for Research on Cancer (IARC) - Agents Classified by the IARC Monographs
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## 4,4'-DIPHENYLMETHANE DIISOCYANATE (MDI) IS FOUND ON THE FOLLOWING REGULATORY LISTS

China Inventory of Existing Chemical Substances China Inventory of Hazardous Chemicals (Chinese)	China Occupational Exposure Limits for Hazardous Agents in the Workplace International Agency for Research on Cancer (IARC) - Agents Classified by the IARC Monographs
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## National Inventory Status

National Inventory	Status
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## WANNATE PM-200

Australia - AICS	Yes
Canada - DSL	Yes
Canada - NDSL	No (polymeric diphenylmethane diisocyanate; 4,4'-diphenylmethane diisocyanate (MDI))
China - IECSC	Yes
Europe - EINEC / ELINCS / NLP	No (polymeric diphenylmethane diisocyanate)
Japan - ENCS	Yes
Korea - KECI	Yes
New Zealand - NZIoC	Yes
Philippines - PICCS	Yes
USA - TSCA	Yes
Taiwan - TCSI	Yes
Mexico - INSQ	Yes
Vietnam - NCI	Yes
Russia - ARIPS	Yes
<b>Legend:</b>	<p>Yes = All CAS declared ingredients are on the inventory</p> <p>No = One or more of the CAS listed ingredients are not on the inventory and are not exempt from listing(see specific ingredients in brackets)</p>

## SECTION 16 OTHER INFORMATION

<b>Revision Date</b>	05/06/2020
<b>Initial Date</b>	08/11/2018

## SDS Version Summary

Version	Issue Date	Sections Updated
26.25.1.1.1	05/06/2020	Ingredients, Physical Properties, Name

## Other information

Classification of the preparation 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.

The 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.

## Definitions and abbreviations

PC—TWA: Permissible Concentration-Time Weighted Average  
 PC—STEL: Permissible Concentration-Short Term Exposure Limit  
 IARC: International Agency for Research on Cancer  
 ACGIH: American Conference of Governmental Industrial Hygienists  
 STEL: Short Term Exposure Limit  
 TEEL: Temporary Emergency Exposure Limit.  
 IDLH: Immediately Dangerous to Life or Health Concentrations  
 OSF: Odour Safety Factor  
 NOAEL :No Observed Adverse Effect Level  
 LOAEL: Lowest Observed Adverse Effect Level  
 TLV: Threshold Limit Value  
 LOD: Limit Of Detection  
 OTV: Odour Threshold Value  
 BCF: BioConcentration Factors  
 BEI: Biological Exposure Index

## Disclaimer

The information in the SDS applies only for the specified product and does not include mixtures of this product with other substances and mixtures. The SDS provides product safety information for personnel trained to use this product only.

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