


TOSOH CORPORATION

3-8-2, Shiba, Minato-ku, Tokyo 105-8623, Japan
 Phone: +81-3-5427-6340 Fax: +81-3-5427-5378

Date of printing: September 2, 2014
 Version: No. T1
 Date of revision:
 Date of issue: September 2, 2014

Product name: MILLIONATE MR-200
1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name	MILLIONATE MR-200
General description	Polymethylene polyphenyl polyisocyanate
Company Identification	
Company name	TOSOH CORPORATION
Department	Isocyanates Department, Urethane Division
Address	3-8-2, Shiba, Minato-ku, Tokyo 105-8623, Japan
Telephone (Emergency telephone)	+81-3-5427-6343
	(Monday ~ Friday, Japan standard time 9:00 a.m. ~ 6:00 p.m.)

2. HAZARDS IDENTIFICATION
GHS classification of the substance or mixture
Physical Hazards

- Flammable liquids Not classified
- Flammable solids Not applicable

Health Hazards

- Acute toxicity (oral) Not classified
- Acute toxicity (skin) Not classified
- Acute toxicity (inhalation: gas) Not applicable
- Acute toxicity (inhalation: vapour) Not applicable
- Acute toxicity (inhalation: dust, mist) **Category 4**
- Skin corrosion/irritation **Category 2**
- Serious eye damages/eye irritation **Category 2B**
- Respiratory sensitization **Category 1**
- Skin sensitization **Category 1**
- Germ cell mutagenicity Not classified
- Carcinogenicity Not classified
- Reproductive toxicity Not classified
- Specific target organ toxicity; single exposure **Category 3 (Respiratory tract irritation)**
- Specific target organ toxicity; repeated exposure Not classified



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|-------------------------------------|----------------|
| ▪ Aspiration hazard | Not classified |
| Environmental Hazards | |
| ▪ Aquatic toxicity (acute) | Not classified |
| ▪ Aquatic toxicity (chronic) | Not classified |

Section is not listed, it can not be excluded from 'Not applicable' or 'Classification not possible'

GHS label elements including precautionary statements

Symbol :



Signal word : Danger

Hazard statement :

- **Harmful if inhaled**
- **Causes skin irritation**
- **Causes eye irritation**
- **May cause allergy or asthma symptoms or breathing difficulties if inhaled**
- **May cause an allergic skin reaction**
- **May cause respiratory irritation**

Precautionary Statements

Prevention

- Obtain special instructions before use.
- Do not handle until all precautions have been read and understood.
- Keep container tightly closed.
(There is a danger of explosion if the carbon dioxide generated when water enters).
- Not to treat an allergic reaction to a person.
- Use only outdoors or in a well-ventilated area.
- Do not breathe dust/ fume/ gas/ mist/ vapour/ spray.



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- Wear protective gloves/ eye protection/ face protection/ protective clothing (Regulatory authorities, manufacturer or supplier specified). Wash thoroughly after handling.
- If ventilation is not sufficient, wear respiratory protection. (Regulatory authorities, manufacturer or supplier specified.)
- Contaminated work clothing should not be allowed out of the workplace.

Response

- In case of fire: Use dry chemical powder, carbon dioxide, foam, large volumes of water spray.
- If swallowed: Rinse mouth with water. Do not induce vomiting. To contact a doctor immediately.
- If inhaled: Remove victim to fresh air and keep at rest in a position comfortable for breathing. To contact a doctor immediately.
- If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. To contact a doctor immediately.
- If on skin (or hair): Remove/take off immediately all contaminated clothing. Rinse skin with water/shower. To contact a doctor immediately.
- If on skin: Wash with plenty of soap and water.
- Seek medical advice/attention if you feel unwell or if skin irritation or rash occurs.
- After handling, wash your hands.
- If you want to reuse contaminated clothing, wash it.
- Sprayed with a neutralizing agent to neutralize or remove adsorbed sand, earth, sawdust, etc.

Storage

- Store container in cool place/ well-ventilated place.

Disposal

- Dispose of contents/container to waste in accordance with local/ regional/ national/ international regulations (to be specified).

3. COMPOSITION/INFORMATION ON INGREDIENTS

Substance / Mixture

Substance



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Chemical name Polymethylene polyphenyl polyisocyanate
(Polymethylene polyphenyl isocyanate)

Contents > 99 %

CAS No. 9016-87-9

【HAZARDOUS INGREDIENT(s)】

Chemical name 4,4'-diphenylmethane diisocyanate (4,4'-MDI)

Contents 44 %

CAS No. 101-68-8

4. FIRST-AID MEASURES

If inhaled

Remove victim to fresh air and keep at rest in a position comfortable for breathing.
Get medical advice/attention immediately.

If on skin

Remove / Take off immediately contaminated clothing and shoes etc. Rinse the part that touches the product, by washing with water or lukewarm water flow. Wash with soap and water. Seek medical advice or attention, if there are change in the appearance or pain persists.

If on eyes

Even if very small contact, rinse with clean water for at least 15 minutes, and seek ophthalmologist's advice/attention. During the eyewash, open the eyelid well with your fingers, then wash well the eyeball and the eyelid with water.

If swallowed

Rinse mouth well. Spit it in person voluntarily if possible, to vomit.
Seek medical advice/attention immediately.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media :

Dry chemical powder, carbon dioxide, foam, large volume of water spray.

Unsuitable extinguishing media : Water jet

Specific hazards during fire :

There is a risk of generating a hazard gas in a fire.

Specific extinction method :

Wear self-contained breathing apparatus and protective gloves, because cracked gas and



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steam are generated in the case of fire. Water is drained off to the drum, container, equipment etc. that have not ignited, and it tries to prevent spreading, overheating and explosion of containers. After the fire is extinguished, neutralize the spilled material with decontaminant. In the meantime, not to enter an outsider.

Special protective for fire-fighters :

In the extinction work, wear self-contained breathing apparatus and protective gloves, because cracked gas and steam are generated.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions :

Wear safety glasses, rubber gloves, a gas mask for organic gas. Restrict entry of unauthorized personnel. To work from the windward. Evacuate people downwind. Better ventilation of the place spilled. Temporary leak repair parts, stop the leak.

Environmental precautions :

Do not flow directly into rivers and sewage spill. Adhered and collected waste material should be promptly disposed of, in accordance with appropriate laws and regulations.

Methods and materials for containment and cleaning up :

(Small spill)

Sprayed with a neutralizing agent to neutralize. Remove adsorbed sand, earth, sawdust, etc. If wiping rags, waste paper, etc., remove and store in a container with a lid.

(Large spill)

As spilled liquid can not spread, enclosed sand, earth, sawdust, etc. Recovered in the liquid container as much as possible. Collection container must not be sealed. Which could not be recovered sprayed with a neutralizing agent to neutralize or Removed by the above method. Wash the spillage area clean with water.

Measures to prevent secondary disasters :

Promptly except near sources of ignition and prepare a fire extinguishing agent. Using a safety tool that does not generate a spark.

7. HANDLING AND STORAGE

Handling

The operator should be trained in handling this product.

Technical measure

Wear appropriate protective goggles, rubber gloves, a gas mask for organic gas. Thoroughly ventilate the workplace, workers wear protective.

Notes



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Those who show allergenic and sensitizing effects should not be in charge.

Safety treatment notes

If a higher pressure in the container, remove the lid and remove the pressure slightly loosen the lid. Do not the filling of container this products to the unwashed containers and attached water containers. Working space is a non smoking. Forbid to use the open flame heating element, high-temperature heating elements.

Storage

Appropriate safekeeping condition

Store in indoors well-ventilated. Keep container tightly closed. Once a container is opened, the container should be sealed with dry nitrogen or dry air (dew point < -30°C) and be closed tightly. If stored outdoors, the container should be covered with waterproof canvas sheet to avoid being exposed in the rain. The use of fire is strictly prohibited in the storage area.

Packaging materials

Excellent corrosion resistance in a suitable material, use containers with airtight packaging. Containers which are prescribe in Fire and Disaster Management Act and UN transport regulations.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Facility and equipment measures

For the use in indoor workplaces, should be structured by the perfectly closed system, or should be established the adequate local exhauster. Provide hand washing and eyewash facility, near the work area, and display the location.

Control limit : Not established

Occupational exposure limits

For 4,4'-diphenylmethane diisocyanate (4,4'-MDI)

JSOH (Japan Society of Occupational Health) : 0.05mg/m³ (TLV-TWA) (2007)

ACGIH : 0.005ppm (0.051mg/m³) (TLV-TWA) (2007)

Personal protective equipment :

Respiratory protection	Respiratory air: JIS T 8155, Gas mask: JIS T 8152, Air-supplied respirator: JIS T 8153
Hand protection	Safety gloves made from rubbers or plastics (impermeable)
Eye protection	Protective glasses with side version or protection goggles



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Skin and body protection Long sleeve work protective clothing

Hygiene measures

Contaminated protective clothing and protective equipment should be replaced as soon as possible. After handling, it is washed one's hands well.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance	Liquid
Color	Yellowish Brown
Odor	Nearly odorless
PH	—
Boiling point	—
Freezing point	—
Flash point	226 °C Cleveland Open Cup
Explosion limit	—
Vapour pressure	< 0.001 Pa at 25°C
Vapour density	—
Specific gravity	1.236 × 10 ³ (kg/m ³) at 25°C
Solubility (water)	Insoluble
Solubility (other)	Soluble in toluene, ethyl acetate or acetone
Octanol/water partition coefficient	—
Viscosity	200 mPa·s at 25°C

10. STABILITY AND REACTIVITY

Stability	Flammability	some
	Ignition quality	na
	Oxidizing	na
	Self-reactive, Explosiveness	na
	Explosive dust	na
	Other	na

Reactivity

Exothermic react with water forming CO₂. Exothermic react with active-hydrogen compound (alcohols, amine and so on). The polymerization reaction with an alkaline substance, a tertiary amine and so on.



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11. TOXICOLOGICAL INFORMATION

For 4,4'-diphenylmethane diisocyanate (4,4'-MDI) =

Monomeric MDI Acute Toxicity (oral) : Not classified

LD50 > 5,000mg/kg P-MDI (contain 50% monomeric MDI) (Wazeter 1964a)

Acute Toxicity (skin) : Not classified

LD50 > 5,000mg/kg P-MDI (contain 50% monomeric MDI) (Wazeter 1964a)

Acute Toxicity (inhalation (gas)) : Not applicable

Monomeric MDI is solid. (by the definition of GHS)

Acute Toxicity (inhalation (vapour)) : Not applicable

Monomeric MDI is solid. (by the definition of GHS)

P-MDI is a liquid with a very low saturated vapour concentration (0.003ppm at 20°C.

Allport et al. 2003). There are no toxicological effects at this concentration.

Acute Toxicity (inhalation (dust, mist)) : Category 4

LC50 (4hr) for respirable mist is 490mg/m³ P-MDI (Appleman and de Jong, 1982).

The mist used in this study meets international guidelines for acute toxicity studies.

But such artificially generated mists are not produced in the workplace and there is no potential exposure to such mists. (EC 2005)

After examination of these data a consensus was reached by EU experts to consider the value inappropriate for classification and labeling, and it was concluded to classify P-MDI as "Harmful" (Directive 67/548/EEC; 25th ATP, Dir 98/8/EC, O.J.30.12.1998). This is equivalent to GHS Category 4.

Skin corrosion /irritation : Category 2

Evidence from animal and man overall indicates slight irritation to skin, one study indicates more severe irritation (EC 2005). EU category irritant (R38).

Serious eye damage/ eye irritation : Category 2B

Several animal studies indicate slight eye irritation. There are some indications of eye irritation. EU category irritant (R36).

Respiratory/skin sensitization

Respiratory : Category 1

Respiratory sensitization demonstrated in animal and man. (EC 2005, Rattray et al. 1994, Vandenplas et al. 1993) EU respiratory sensitizer (R42).

Skin : Category 1

Skin sensitization demonstrated in animal and man. (EC 2005, Thorne et al. 1987, Bernstein et al. 1993). EU skin sensitizer (R43).

Germ cell mutagenicity : Not classified

There are no germ cell mutagenicity data. There are somatic cell mutagenicity data



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(monomeric and P-MDI) in vitro and in vivo and in particular mammalian studies, which are negative. (EC 2005, Seel et al. 1999, Jetoc 1982, Pauluhn et al. 2001)

Carcinogenicity : Not classified

A carcinogenicity study in rats with inhalation exposure to highly respirable mists of P-MDI up to the maximum tolerated dose (Reuzel et al. 1990), revealed effects to the respiratory tract only.

Effects were reflective of irritation and there was a low incidence of pulmonary adenomas and a single adenocarcinoma in the high exposure group only.

Another long term exposure study using an unusual protocol (17 hours per day exposure) with monomeric MDI also revealed an irritative effect with some pre-neoplastic changes in the highest exposure group. (Hoymann et al. 1995)

Overall these studies indicate that long term lung irritation to MDI mists results in a hyperplasia leading eventually to adenoma formation. Such high concentrations and highly respirable mists are only possible in the laboratory, and the inapplicability of this finding to human exposure to MDI vapour at low concentration in the workplace, results in a “not classified” for carcinogenicity.

It is noted that IARC classification is group 3. (IRAC 1999)

Epidemiological studies of MDI exposed workers show no increased carcinogenicity related to MDI exposure.

As the conclusion of the document in Germany MAK (MAK-Values Vol.45, 2008), it sets the MAK value of MDI to category 4 (Carcinogen: substance is not genotoxic or genotoxic activity is negligible substance.)

Reproductive toxicity : Not classified

Studies are negative at P-MDI containing about 50% monomeric MDI.

Specific target organ toxicity-single exposure : Category 3

For animals, transient irritative effects are reported at monomeric MDI and P-MDI. (Weyel and Schaffer 1985, Pauluhn et al. 1999, Pauluhn 2000, Kilgour et al. 2002)

For humans, the low vapour pressure of MDI means that concentrations that may be expected to be irritative are rarely reached. However, MDI may be expected to be irritating at concentrations above the recommended exposure limits.

Specific target organ toxicity-repeated exposure : Not classified

Lung decrement has been reported in some studies as a consequence of repeated exposure to MDI. However, this effect can only be observed after inhalation exposure in the tissue at the point of contact and does not represent systemic toxicity. It is a local effect that is already covered by respiratory irritation (TOST single exposure, Category 3) and respiratory sensitization (Category 1).

In humans some, but not all epidemiological studies have found long term decreases in



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ventilatory function and respiratory symptoms. (EC 2005)

However there is generally co-exposure to other materials and sometimes also to TDI.

For TDI Ott(2002) and Ott, Diller and Jolly(2003), indicate that respiratory sensitisation may have contributed to the lung decrement reported in some studies.

Therefore, it is concluded that possible lung effects do not qualify as specific target organ systemic toxicity after repeated exposure in accordance to chapter 3.9.1.6. of the GHS (UNECE 2003).

Aspiration Hazard : Not classified

12. ECOLOGICAL INFORMATION

For 4,4'-diphenylmethane diisocyanate (4,4'-MDI) = Monomeric MDI

Aquatic Toxicity (acute) : Not classified

LC50 for fish, invertebrates and algae > 1,000mg/L

Aquatic Toxicity (chronic) : Not classified

NOEC > 1,640mg/L (Blom and Olderrama, 1994)

13. DISPOSAL CONSIDERATIONS

The remainder waste (Disposal of this product)

Dispose of contents/container to waste treatment company having the official approval of laws and regulation. Disposed of as a solid form by reacting a polyol. Stirring the liquid neutralizing agent, was added dropwise and allowed to stand for 2 days this product, detoxified changed to urea compound. Incinerated in appropriate facilities.

Pollution container and packing

Empty container filled with water and allowed to stand for 2 days (Should not be sealed), then, disconnect the water. Neutralizing agent to put the container, and processes to be washed after neutralizing. Used container should be punctured and scrapped, so that it is not used for any other purpose.

14. TRANSPORT INFORMATION

International Regulations

Land : Transport in accordance with your country and regions regulations.

(RID, ADR, DOT etc.)

Sea : Transport in accordance with IMDG Code.

Air : Transport in accordance with ICAO-TI/ IATA-DGR.



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UN number : Not applicable
Proper shipping name : - (Polymethylene polyphenyl isocyanate)
Hazard class : Not applicable
Packing group : Not applicable
Marine Pollutant : Not applicable
IMDG class : Not applicable

Follow all the regulations in your country. Be sure that the container is tightly sealed, that no leakage is found and that all the necessary indications are specified. Filling, loading and extracting operations should be performed under the supervision of an authorized operator. Nitrogen gas or dry air should be charged into the container for transportation after filling or extracting.

Ship hazardous materials transportation and storage regulations based on the Ship Safety Act: It corresponds to "poison" hazardous materials, if you want to maritime transport, and transport you necessity to take measures in accordance with the law Ship Safety.

15. REGULATORY INFORMATION

Regulatory information with regard to this substance in your country should be examined by your own responsibility.

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