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## MATERIAL SAFETY DATA SHEET (JURA Model)

### 1. CHEMICAL PRODUCT & COMPANY IDENTIFICATION

#### CHEMICAL PRODUCT

Product name : Polymeric MDI

Other means of identification : Polymethylene polyphenylene polyisocyanate ; PMDI

#### COMPANY IDENTIFICATION

Company name : Japan Urethane Raw Materials Association

Address :

Department :

Telephone :

Emergency telephone :

Fax :

e-mail address :

MSDS № : 0334

#### RECOMMENDED USE OF THE CHEMICAL AND RESTRICTIONS ON USE :

The main use is polyurethane raw materials ( flexible and semi-rigid foam, rigid foam, elastomer, and paint, glue, binder, etc ).

### 2. HAZARD IDENTIFICATION

#### GHS CLASSIFICATION OF THE SUBSTANCE OR MIXTURE

##### PHYSICAL HAZARDS

- Explosives : Not applicable
- Flammable gases : Not applicable
- Flammable aerosols : Not applicable
- Oxidizing gases : Not applicable
- Gases under pressure : Not applicable
- Flammable liquids : Not classified
- Flammable solids : Not applicable
- Self-reactive substances and mixtures : Not applicable
- Pyrophoric liquids : Not classified
- Pyrophoric solids : Not applicable
- Self-heating substances and mixtures : Not classified
- Substances and mixtures which, in contact with water, emit flammable gases : Not classified
- Oxidizing liquids : Not classified
- Oxidizing solids : Not applicable
- Organic peroxides : Not applicable

- Corrosive metals : Not classified

**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
- Aspiration hazard : Not classified

**ENVIRONMENTAL HAZARDS**

- Aquatic toxicity (acute) : Not classified
- Aquatic toxicity (chronic) : Not classified

**GHS LABEL ELEMENTS, INCLUDING PRECAUTIONARY STATEMENTS****SYMBOL**

**SIGNAL WORD : Danger**

**HAZARD STATEMENT**

- Harmful if inhaled
- Causes skin irritation
- Causes serious eye irritation
- May cause allergy or asthma symptoms or breathing difficulties if inhaled
- May cause respiratory irritation

**PRECAUTIONARY STATEMENT****【Prevention】**

- Do not handle until all safety precautions have been read and understood.
- Obtain special instructions before use.
- Do not eat, drink or smoke when using this product.
- Wear respiratory protection/protective gloves / protective clothing / eyes protection / face protection.

- Use only outdoors or in a well-ventilated area.
- Do not breathe dust / fume / mist.
- Wash hands thoroughly after handling.
- Contaminated work clothing should not be allowed out of the workplace.
- Keep away from any possible contact with water and alkali.

**【Response】**

- If inhaled : Remove victim to fresh air and keep at rest in a position comfortable for breathing.
- If swallowed: Rinse mouth with water. Do not induce vomiting.
- If in eyes : Rinse cautiously with water for 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
- If on skin : Wash with plenty of soap and water.
- If skin irritation occurs, get medical advice/attention.
- Take off contaminated clothing and wash before reuse.
- Get medical advice/attention if you feel unwell.
- In case of fire: Use powder, carbon dioxide, foam for extinction. When a fire is spread, large volumes of spray water should be used.
- When leaking out, collect as much as possible to the container and so on. After that, spray and neutralize with an ammonia water, alcohol and so on, and then absorb it with sands.
- If exposed or concerned : Get medical attention/advice.

**【Storage】**

- Store in a dry place. Keep container tightly closed in the locked 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

CHEMICAL NAME : Polymethylene polyphenylene polyisocyanate

PURITY : > 98%

METI № : (7)-872

\* Class Reference № in The Gazetted List (for Existing Chemical Substances)

ISHA № : Existing (A chemical substance for which public notice has been given by METI № to 1979 June 29th)

\* Class Reference № in The Gazetted List (Industrial Safety and Health Act)

CAS № : 9016-87-9 (Isocyanic acid, polymethylenepolyphenylene ester)

HAZARDOUS INGREDIENT(s) : Diphenylmethane-4,4'-diisocyanate (or 4,4'-MDI) 30~70%

**4. FIRST-AID MEASURES****IF INHALED**

- Remove victim to fresh air and keep at rest in a position comfortable for breathing.
- Get medical attention / advice immediately.
- When breathing stops, give an artificial respiration after securing the loosening respiratory tract in the

clothing.

- Get medical advice/attention immediately when the cough and phlegm, etc. are awful.

#### IF ON SKIN

- Wash off with soap and water immediately.
- Remove/Take off immediately all contaminated clothing.
- If skin irritation or rash occurs, get medical advice/attention.
- Take off contaminated clothing and wash before reuse.

#### IF IN EYES

- Even if very small amount contact, rinsing by clean water for at least 15 minutes, and get ophthalmologist's examination.
- Remove contact lenses, if present and easy to do. Continue rinsing.
- If eye irritation persists, get medical advice/attention.

#### IF SWALLOWED

- After rinse mouth immediately with water, give about 250 ml of water or milk to thin in the stomach, and do not induce to vomit.
- Moreover, do not give anything by mouth to the patient when not conscious.
- Receive the doctor's treatment (stomach pump) promptly.

## 5. FIRE-FIGHTING MEASURES

SUITABLE EXTINGUISHING MEDIA : Carbon dioxide, dry chemical powder, foam, water spray in case of larger fires.

UN SUITABLE EXTINGUISHING MEDIA : Water jet

#### SPECIFIC EXTINCTION METHOD

- For initial stage extinction, carbon dioxide or dry chemical powder.
- When a fire extends, extinguished by a large amount of water spray.
- Water is drained off to the drum, container etc. that have not ignited, and it tries to prevent fire spreading, overheating, and explosion of containers.
- After the fire is extinguished, neutralize the spilled material with decontaminant.

#### SPECIAL PROTECTIVE FOR FIRE-FIGHTERS

- Because during a fire, isocyanate vapour may be generated, firemen have to wear self-contained breathing apparatus and other protective equipment like helmet, gloves etc.

## 6. ACCIDENTAL RELEASE MEASURES

#### PERSONAL PRECAUTIONS, PROTECTIVE EQUIPMENT AND EMERGENCY PROCEDURES

- Evacuate personnel without wearing protective equipment. Put on protective equipment. Ensure adequate ventilation.

#### ENVIRONMENTAL PRECAUTIONS

- Avoid release to the environment.
- Certain the spill to prevent spread into drains, sewers or rivers

#### METHODS AND MATERIALS FOR CONTAINMENT AND CLEANING UP

- Neutralize the residues with decontaminant.
- Wash the spillage area clean with water.

- Large spill : Admix with sand, clay or sawdust to prevent the spillage/leakage from further spreading out.
- The floor after collection catches disposal of the neutralization as above-mentioned and the detoxification.
- Do not tightly close waste containers (CO<sub>2</sub> formation !).  
Waste should be disposed of as described in chapter "13. DISPOSAL CONSIDERATION".
- An example of decontaminant solution;  
Water / Sodium carbonate / Liquid detergent = 90-95 / 5-10 / 0.2-2 (by weight)

## 7. HANDLING AND STORAGE

### HANDLING

#### TECHNICAL MEASURE

- Wear protective equipment measures described in "Chapter 8. EXPOSURE CONTROL / PERSONAL PROTECTION", and wear an appropriate protective equipment.
- The local exhaust device is set up in the indoor handling.
- Specifically, in the case of heated MDI and handling a powder, wear an appropriate guard and prevent direct contact.

#### LOCAL-VENTILATION/WHOLE-VENTILATION

- Set the local exhaust or general ventilation as mentioned in "Chapter 8. EXPOSURE CONTOROLS / PERSONAL PROTECTION".

### NOTES

- Obtain special instructions before use.
- Do not handle until all safety precautions have been read and understood.
- Do not contact/breathe/swallowing.
- Wash hands thoroughly after handling.
- Use only outdoors or in a well-ventilated areas.
- Contaminated work clothing should not be allowed out of the workplace.
- Do not eat, drink or smoke when using this product.

### SAFETY TREATMENT NOTES

- Pay attention to avoid contact with water or substance which react with MDI.
- Always has a stock of enough personal protectors and decontaminant so solution available for emergency.
- Take care of falling or tumble for handling containers.

CONTACT AEVASION : Refer to "Chapter 10. STABILITY AND REACTIVITY".

### STORAGE

#### TECHNICAL MEASURE

- An indoor storehouse should be built by a fireproof construction and having well ventilation.
- Its floor should be made of impermeable materials.
- The equipment of a lighting and a lighting necessary to handle it is installed.

#### APPROPRIATE SAFEKEEPING CONDITION

- Store container tightly closed in well-ventilated areas.
- Store locked up.

- Once a container is opened, the container should be sealed with dry nitrogen or dry air (dew point < -30°C) and be closed tightly.

INCOMPATIBLE SUBSTANCES : Refer to "Chapter 10. STABILITY AND REACTIVITY".

PACKAGING MATERIALS : containers which are prescribed in Fire and Disaster Management Act and UN transport regulations.

## 8. EXPOSURE CONTROLS / PERSONAL PROTECTION

### FACILITY AND EQUIPMENT MEASURES

- Facilities in where this material is handled should be structured by the perfectly closed system.  
Should be established the adequate local exhauster in the indoor working area where steam or the mist occurs.
- The worker should wear an appropriate protective equipment  
Make available emergency safety shower and eye wash in the work area.  
The floor should be made of impermeable materials.

CONTROL LIMIT : Not established

### OCCUPATIONAL EXPOSURE LIMITS

- JSOH : TLV-TWA 0.05 mg/m<sup>3</sup> (4,4'-MDI) (2009)<sup>8)</sup>  
\* JSOH : Japan Society of Occupational Health
- ACGIH : TLV-TWA 0.005ppm (0.051 mg/m<sup>3</sup>) (4,4'-MDI) (2010)<sup>9)</sup>  
\* ACGIH : American Conference of Governmental Industrial Hygienists  
\* TLV-TWA : Threshold Limit Value - Time Weighted Average

### PERSONAL PROTECTIVE EQUIPMENT

- Respiratory protection :  
Compressed air open-circuit self-contained breathing apparatus (JIS T 8155)  
Supplied-air respirators (JIS T 8153)
- Hand protection : Protective gloves made from rubbers or plastics.
- Eye protection : Protective glasses with shroud, goggles
- Skin and body protection : Long sleeve protective clothing and safety shoes.

### HYGIENE MEASURES

- Wash hands thoroughly after handling.
- Contaminated work clothing should not be allowed out of the workplace.

## 9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance : dark-brown liquid

Odour : nearly odourless

pH : No data

Boiling point : > 300°C<sup>10)</sup>

Freezing point : ???

Flash point : 208°C (COC)<sup>10)</sup>

Explosion properties : No data

Vapour pressure : 4×10<sup>-4</sup>Pa (25°C)

Vapour density (air=1) : 8.5 (4,4'-MDI)

Specific gravity : approx. 1.22 (43°C)

Solubility : Insoluble in water.

Soluble in common organic solvents as ketone and ester.

Octanol/water partition coefficient : No data

Auto-ignition temperature : No data

Decomposition temperature : No data

Viscosity : 100~250 mPa·s (25°C) <sup>10)</sup>

## 10. STABILITY AND REACTIVITY

STABILITY : In a usual handling condition, chemically stable against light, heat, and impact.

### REACTIVITY

- Exothermic react with amines, water and alcohols.
- Exothermic homo-polymerization itself in the presence of basic substance or certain metal compound.
- React with water forming CO<sub>2</sub>.

### POSSIBILITY OF HAZARDOUS REACTIONS

- Exothermic reaction with active-hydrogen compound (water, alcohols, amine and so on ). Reacts with water forming CO<sub>2</sub>, in closed containers, risk of bursting owing to increase of pressure.

### INCOMPATIBLE MATERIALS

- Copper, and these alloys, aluminum, polyvinyl chloride

### HAZARDOUS DECOMPOSITION PRODUCTS

- Nitrogen compounds

## 11. TOXICOLOGICAL INFORMATION

ACUTE TOXICITY [ORAL] : Not classified

LD50 > 5000mg/kg PMDI (Wazeter 1964a) <sup>32)</sup>

ACUTE TOXICITY [SKIN] : Not classified

LD50 > 5000mg/kg PMDI (Wazeter 1964b) <sup>33)</sup>

ACUTE TOXICITY [INHALATION (GAS)] : Not applicable

PMDI is liquid

ACUTE TOXICITY [INHALATION (VAPOUR)] : Not applicable

PMDI is a liquid with a very low saturated vapour concentration (0.003ppm at 20°C, Allport et al. 2003 <sup>11)</sup>). There are no toxicological effects at this concentration.

ACUTE TOXICITY [INHALATION (DUST, MIST)] : Category 4

The 4-hour LC<sub>50</sub> for respirable aerosols is 490 mg/m<sup>3</sup> PMDI (Appleman and de Jong, 1982 <sup>12)</sup>).

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

But such artificially generated aerosols are not produced in the workplace and there is no potential exposure to such aerosols (EC 2005 <sup>16)</sup>).

After examination of these data a consensus was reached by EU experts to consider the value inappropriate for classification and labelling, and it was concluded to classify PMDI as “Harmful” (Directive 67/548/EEC; 25<sup>th</sup> ATP <sup>15)</sup>, Dir 98/8/EC, O.J. 30.12.1998 <sup>15)</sup>).

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 <sup>16)</sup>). EU category irritant (R38).

**SERIOUS EYE DAMAGES/EYE IRRITATION : Category 2B**

Several animal studies indicate slight eye irritation. There are some indications of human eye irritation.

EU category irritant (R36).

**RESPIRATORY SENSITIZATION : Category 1**

Respiratory sensitisation demonstrated in animal and man. (EC 2005 <sup>16)</sup>, Pauluhn 1997 <sup>27)</sup>, Vandenplas et al. 1993 <sup>31)</sup>). EU respiratory sensitiser (R42).

**SKIN SENSITIZATION : Category 1**

Skin sensitisation by monomeric MDI demonstrated in animal and man. (EC 2005 <sup>16)</sup>, Thorne et al. 1987 <sup>29)</sup>, Bernstein et al. 1993 <sup>31)</sup>). EU skin sensitiser (R43).

**GERM CELL MUTAGENICITY : Not classified**

There are no germ cell mutagenicity data. There are somatic cell mutagenicity data (monomeric and PMDI) in vitro and in vivo and in particular mammalian studies, which are negative. (EC 2005 <sup>16)</sup>, Seel et al. 1999 <sup>28)</sup>, JETOC 1982 <sup>19)</sup>, Pauluhn et al. 2001 <sup>26)</sup>).

**CARCINOGENICITY : Not classified**

A carcinogenicity study in rats with inhalation exposure to highly respirable aerosols of PMDI up to the maximum tolerated dose (Reuzel et al. 1990 <sup>27)</sup>), 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 <sup>17)</sup>).

Overall these studies indicate that long term pulmonary irritation to MDI aerosols results in a hyperplasia leading eventually to adenoma formation.

Such high concentrations and highly respirable aerosols are only possible in the laboratory, and the inapplicability of this finding to human exposure to MDI vapour at low concentration results in a “not classified” for carcinogenicity.

It is noted that IARC classification is group 3, (IARC 1999 <sup>18)</sup>).

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<sup>35)</sup>), it sets the MAK value of MDI to category 4 (Chemicals known to act typically by non-genotoxic mechanisms).

**REPRODUCTIVE TOXICITY : Not classified**

Developmental studies negative.

**SPECIFIC TARGET ORGAN TOXICITY-SINGLE EXPOSURE : Category 3**

For animals transient irritative effects are reported data (monomeric and PMDI, eg Weyel and Schaffer 1985 <sup>34)</sup>, Pauluhn et al. 1999 <sup>24)</sup>, Pauluhn 2000 <sup>25)</sup>, Kilgour et al. 2002 <sup>20)</sup>).

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, Cat. 3) and respiratory sensitization (Category 1).

In humans some, but not all epidemiological studies have found long term decreases in ventilatory function and respiratory symptoms (EC 2005 <sup>16)</sup>).

However there is generally co-exposure to other materials and sometimes also to the diisocyanate toluene diisocyanate. For this diisocyanate Ott (2002) <sup>21)</sup> and Ott, Diller and Jolly (2003) <sup>22)</sup>, 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 <sup>30)</sup>).

In addition, all warning and safety measures for local effects as well as for acute inhalation toxicity category 1 already provide for the protection of workers and professional users that are involved in the handling of MDI.

ASPIRATION HAZARD : Not classified

Not applicable.

## 12. ECOLOGICAL INFORMATION

AQUATIC TOXICITY [ACUTE] : Not classified

LC<sub>50</sub> for fish, invertebrates and algae > 1000 mg/L.

AQUATIC TOXICITY [CRONIC] : Not classified

NOEC >1640 mg/L (Blom and Oldersma 1994 <sup>14)</sup>)

## 13. DISPOSAL CONSIDERATIONS

THE REMAIDER WASTE

- Dispose of contents/container to waste treatment company having the official approval of laws and regulations.
- After danger and the hazardous properties are notified thoroughly to waste treatment company, processing is consigned when the processing of waste is consigned.
- MDI also was contaminated after processing in open system using non-toxic and neutralizing agent, appropriate disposal methods.

POLLUTION CONTAINER AND PACKING

- The container is recycled after cleaned, or is disposed of appropriately according to the standard of related laws and regulations and the local government regulations.
- Remove contents completely in case of disposal of an empty container.

## 14. TRANSPORT INFORMATION

INTERNATIONAL REGULATIONS

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

Sea : Transport in accordance with IMDG Code.

UN Number : Not applicable

UN Classification : Not applicable

Domestic regulations : Transport in accordance with local regulation.

Land : Follow the mode of transportation as provided in the Fire and Disaster Management Act, Industrial Safety and Health Act, Road Vehicles Act, etc.

Sea : Follow the mode of transportation as provided in the Ships Safety Act.

Air : Follow the mode of transportation as provided in the Aviation Law.

Emergency response guideline number : Not applicable

## 15. REGULATORY INFORMATION

Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc

- Type II Monitoring Chemical Substance : 4,4'-MDI

Industrial Safety and Health Act

- Notifiable substances : 4,4'-MDI  
(Article 57-2 of Act, appended table 9 of article 18 of Order)
- Mutagenicity substances (guideline and notification substances) : 4,4'-MDI

Labor Standards Act

- Illness chemical substances : MDI  
items 4-1 in appended table 1-2 of Ordinance 35

Public notice of the Ministry of Health and Welfare No. 36 of March 30, 1978

Act on Confirmation, etc. of Release Amounts of Specific Chemical Substances in the Environment and Promotion of Improvements to the Management Thereof (PRTR law)

- Class 1 Designated Chemical Substances : 4,4'-MDI  
(Cabinet Order №1-448)

Fire and Disaster Management Act (Fire Service Law)

- Dangerous Substances : Class 4-4

Act Relating to the Prevention of Marine Pollution and Maritime Disaster

- Harmful liquid Substances (appended table 1 of Order) : Category Y

Air Pollution Control Act

- Substances of possibility to correspond to Hazardous Air Pollutant : 4,4'-MDI (№221)

## 16. OTHER INFORMATION

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All specifications are to be created based on the information we can get at this time may be revised by new knowledge.

The content, the physico-chemical property and so on are not a guaranteed-performance.

Notes are usually aimed at handling. If special handling, usage, please Usage for safety measures.

## CONTACT

Company :

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