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**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

MDI POLYOL PREPOLYMER

This Assessment has been compiled in accordance with the provisions of the *Industrial Chemicals (Notification and Assessment) Act 1989* and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by Worksafe Australia which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Arts, Sport, the Environment and Territories and the assessment of public health is conducted by the Department of Health, Housing and Community Services.

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT**MDI POLYOL PREPOLYMER****1. APPLICANT**

Dow Chemical (Australia) Ltd, Kororoit Creek Road, Altona,
Victoria 3018

2. IDENTITY OF THE CHEMICAL

Based on the nature of the chemical and the data provided, MDI polyol prepolymer is not considered to be hazardous. Therefore the details of chemical identity, monomers, spectra, molecular weight and molecular and structural formulae have been exempted from publication in the Full Public Report and the Summary Report.

Other names: MDI-polyol prepolymer;
isocyanate terminated adduct

Trade names XUS-15015.00 Experimental RIM Chemical
Spectrim (R) 25A Isocyanate
Spectrim (R) 35A Isocyanate
Spectrim (R) 50A Isocyanate

Number-average molecular weight: > 1000

Maximum percentage of low molecular weight species (molecular weight < 1000): maximum of 40% between 500-1000;
none below 500.

3. PHYSICAL AND CHEMICAL PROPERTIES

The properties mentioned in this section refer to the "product" containing the notified chemical rather than to the "new polymer" (MDI-polyol prepolymer). The MDI-polyol prepolymer is prepared with an excess of MDI and is not isolated from this component at any stage. The notified chemical is imported as part of the "product" containing diphenylmethane diisocyanate and additive.

Appearance at 20°C and 101.3 kPa:	Pale yellow liquid
Odour:	none mentioned
Boiling Point:	200 °C at 14 Pa (this may be MDI)
Glass-transition Temperature:	Not available
Specific Gravity:	1.1561 @ 25°C
Vapour Pressure:	6.6×10^{-7} kPa at 25°C
Water Solubility:	The MDI reacts with water to form an insoluble urea and large quantities of carbon dioxide. It is also expected to react with water to form 4,4'-methylenedianiline (12).
Fat Solubility:	Not available
Hydrolysis as a function of pH:	This property could not be measured as MDI reacts slowly with water releasing carbon dioxide and forming insoluble polyureas.
Partition Co-efficient: (n-octanol/water)	These parameters were not measured because MDI in the polymer mixture reacts with water
Adsorption/Desorption:	to form polyureas and reacts with octanol to form
Dissociation constant:	polyurethanes

Flash Point: > 182°C, closed cup

Flammability Limits: Not determined. MDI is classified as combustible liquid. In the presence of an existing fire or heat source sufficient to cause vaporization of the liquid, and adequate oxygen, isocyanates will burn.

Combustion Products: At > 260°C combustion products include MDI vapours/mist, carbon dioxide, carbon monoxide, nitrogen oxides and traces of hydrogen cyanide.

Decomposition Temperature: MDI decomposes at > 260°C

Decomposition Products: Hazardous decomposition products include isocyanate vapour and mist, carbon dioxide, carbon monoxide, nitrogen dioxides and traces of hydrogen cyanide.

Autoignition Temperature: Does not self ignite.

Explosive Properties: MDI will not detonate as a result of heat, shock, or friction. Under normal storage and processing conditions, the relatively low vaporization characteristics of MDI minimize the hazard of explosion. Under fire conditions when the MDI vapour is generated, an explosion may occur. Explosive limits for MDI have not been determined.

Reactivity/Stability: The "product" is stable under normal conditions. However prolonged heating above 71°C or storage below 24°C will initiate self polymerization of the material involving the formation of dimers and trimers.

MDI and therefore the "product" will react with water, acid, base, alcohols, metal compounds, and surface active materials. Water will react with MDI to

form heat, carbon dioxide, and insoluble urea. The combined effect of the carbon dioxide and heat can produce an increase in pressure sufficient to rupture a closed container.

Particle size distribution: not applicable the product is present as liquid.

4. PURITY OF THE CHEMICAL

Degree of purity : the imported product contains 30% of the notified polymer

Toxic or hazardous impurities:

Chemical name:	1,1'-methylene bis (isocyanatobenzene)
Synonym(s) :	MDI
CAS No.:	26447-40-5
Weight percentage:	>50%
Toxic properties:	data are available on an MDI isomer, CAS 101-68-8, which has the following properties: Irritating to the eyes and respiratory system, may be sensitising on skin contact, harmful by inhalation. (2) LC ₅₀ in rat = 178 mg/m ³ (2). Worksafe Australia National Exposure standard for all isocyanates: TWA = 0.02 mg/m ³ , STEL = 0.07 mg/m ³ (1)

This residual monomer is always present and contributes to the hazard of the chemical.

Non-hazardous impurities: (> 1% by weight): none

Additive/Adjuvant:

The additive contained in the final product is considered less hazardous than the MDI component. Precautions to protect against MDI will protect against this chemical (the identity of which has therefore been exempted from publication in the Full Public Report and the Summary Report).

5. INDUSTRIAL USE

The notified chemical will be imported as the "product" consisting of the "new polymer", excess MDI and an additive. The "new polymer" is produced in a reaction tank with excess MDI, and is at no stage isolated from this mix, will be imported largely to replace other MDI products already in use. The notified chemical in the product will be used in the production of polyurethane elastomers for industrial components. It is estimated that >10 tonne of the product (corresponding to amount >3 tonne notified chemical) will be imported per year for the first 5 years.

The notified MDI polyol prepolymer has been manufactured in the USA for 7 years.

6. OCCUPATIONAL EXPOSURE

Transport and Storage:

The product containing the notified MDI polyol prepolymer, will be transported by sea from the USA in heated containers. Each shipment comprises 36 drums containing a total of 10 tonnes of the product (3 tonnes of the notified chemical). The container is transported from the wharf to a dangerous goods store (approved by the Victorian Occupational Health and Safety Authority) by road where drums are transferred into dedicated storage containers and maintained at 30°C. The substance is classified as a dangerous good under the Australian Code for the Transport of Dangerous Goods by Road and Rail (3). The drums will be transported by road, in pallet loads of four drums, by trucks licensed to carry dangerous goods. There is potential for human exposure to the product containing the notified chemical if the appropriate safety procedures are not observed.

Customer development work

The notified chemical will be used for product development work involving approximately 3 trials in a year. Each trial is anticipated to involve 3 consecutive days and 6 hours per day.

The product is to be processed in a closed system polyurethane dispensing machine. Polyol and isocyanate reactants flow into a mixing chamber. The two streams are injected directly into a

closed mould cavity. A similar process is used at the customer plant.

Heating isocyanate based products causes high vapour concentrations. On cooling these vapours, a condensate and airborne droplets may be formed, with occupational exposure occurring unless the appropriate ventilation and protective equipment is used.

There are several activities that may result in occupational exposure. These include:

- . pumping or pouring the liquid product isocyanate directly from a 208 L drum into the machine's isocyanate tank at 25°C.
- . flushing out isocyanate previously used in the machine. The product is circulated around the machine at high pressure and the flushed material is then emptied into a 208 L drum and labelled.
- . Processes where vaporous MDI is produced. These include instances:
 - when the machine tank is depressurised prior to filling with fresh product; and
 - when the mould is removed and the combination of the mould temperature (60-70°C) and heat of reaction (>100°C) promotes the release of vapours.

The vapours are captured by an extension of the local exhaust ventilation system.

A personal monitoring system for all isocyanates is being established for all users of isocyanate products.

End use in manufacturing

The product containing the notified chemical is to be mixed with a polyol reactant to fill a mould to make automotive parts. The process is essentially the same as that used in the Dow Facility. No by-products will be formed in this process.

Worker exposure is expected by the notifier to be 'minimal' when closed systems are used and recommendations for ventilation and protective gear are followed.

7. PUBLIC EXPOSURE

MDI is listed in the Australian Inventory of Chemical Substances and is covered by the Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG code) (3). Since this compound is present in excess in the MDI-polyol prepolymer product, transport of the product is to be pursuant to the ADG code. Liquid waste is to be disposed of by a company licensed to incinerate MDI liquid. Solid waste will be sent to an approved landfill site for burial. Used container drums will be decontaminated by water prior to disposal (landfill or drum recycling) and rinse fluids will be disposed of according to state regulations (eg. treatment in an approved waste water facility). Public exposure to the raw material will therefore be low. During the production of manufactured goods, MDI-polyol prepolymer is further polymerised, forming polyurethane elastomers, resulting in negligible public exposure.

8. ENVIRONMENTAL EXPOSURE

. Release

The notified product is stated to replace existing MDI based prepolymer products currently used for this purpose.

MDI-polyol prepolymer will be processed at the two sites utilising a closed system reaction injection moulding machine. This involves emptying the product drums into the machine's reservoirs, injecting liquid product and further polyol to an enclosed pressurised mould cavity where polymerisation occurs to endpoint/curing after a few minutes. When the moulded polyurethane elastomer components are removed from the mould, the notified substance is considered to be fully reacted.

In the event of accidental spillage, the 1,1'-methylenebis (isocyanatobenzene) (MDI) component of MDI-polyol prepolymer could cause an immediate terrestrial or aquatic environmental hazard. Contamination of drains or water ways should be avoided by containing and absorbing the polymer mixture with wet sand or soil.

Given the reactivity of MDI in water, the likely environmental hazard will abate rapidly with the formation of water insoluble polyurea.

From the environmental perspective, given the low vapour pressure of the notified substance, atmospheric contamination during the use of MDI-polyol prepolymer to make polyurethane elastomer mouldings is unlikely.

Waste generated from the above processes are expected to be minimal and will come from two sources :

- off-cuts from trimming the polyurethane moulding are not mentioned in the submission but would be expected. Solid waste will be disposed of to landfill or by incineration by Victorian EPA licensed contractors. The water insoluble polyurethane waste is not expected to be mobile or undergo degradation in the environment.
- polymer residue from drums. This residue can be converted to water insoluble polyureas and polyurethanes by reaction with water and disposed of to landfill or by incineration by Victorian EPA licensed contractors.

The empty product drums, after triple rinsing, can be punctured to prevent reuse and disposed of to landfill or sent, undamaged, to an approved drum reconditioner or recycler.

. **Fate**

The notifier states that by nature of its application and the durability required of the finished product, the polymer is required to be stable under a wide range of conditions.

The polymer will form oxides of carbon and nitrogen, hydrocarbon fragments and water vapour on combustion.

MDI-polyol prepolymer residues from containers will be converted to water insoluble polyureas and polyurethanes and, as such, are not expected to hydrolyse or biodegrade in landfill conditions.

9. **EVALUATION OF TOXICOLOGICAL DATA**

Under the *Industrial Chemicals (Notification and Assessment) Act, 1989* (the Act), toxicity data is not required for polymers with

an average number molecular weight >1000. the material safety data sheet for the product addressed the hazards of the free diisocyanate The data was summarised in the submission and is again summarised in this report. References given are those cited in the notification statement.

Acute oral toxicity is reported to be very low. The LD₅₀ in rats has been found to be > 15 g/kg body weight. Ingestion may cause gastrointestinal injury. (4)

Human exposure to the vapour or aerosol may cause irritation to the upper respiratory tract and lungs and cause respiratory sensitisation. Symptoms may not appear until several hours after exposure (5,6,7). Sensitisation may occur after a single high exposure to MDI but it usually results from repeated exposures. There is no known threshold for the sensitisation process and exposure to MDI at levels below the exposure standards may cause allergic symptoms in individuals already sensitised. Cross sensitisation is known to occur (8).

Prolonged contact with the skin is essentially non-irritating. However, material may stick to the skin and cause irritation upon removal. Skin contact may result in allergic/sensitised skin reactions or respiratory sensitisation (5,9) but is not expected to result in absorption of amounts sufficient to cause other adverse affects. Cross sensitisation to other related MDI materials may occur.

Brief contact with low concentrations of MDI vapour or aerosol are essentially non-irritating to the eye. Higher concentrations may cause irritation and pain. When MDI or MDI-containing products have been splashed into the eye they form a thick material which is difficult to remove from the eye and eyelid. The final outcome of these incidences has been, at worst, slight conjunctival irritation (10,11)

MDI has been found to be mutagenic in the Ames test to *Salmonella typhimurium* strains TA98 and TA100 in both the presence and absence of a microsome activation system (Anderson *et al* as cited in (3). Technical grade (purity 45%) MDI has been found to induce chromosome aberrations in the absence of metabolic activation in human whole blood lymphocyte cultures (12). However, the notifier reports that mutagenicity data on MDI is inconclusive. Dow claims that *in vitro* studies suggest that MDI

is weakly mutagenic and that there have been no positive findings in 'valid' studies carried out *in vivo* (12,13,14).

10. **ASSESSMENT OF ENVIRONMENTAL EFFECTS**

No ecotoxicological data were provided, which is acceptable for polymers of NAMW > 1000 according to the Act.

However, ecotoxicological results were provided for MDI, considered a hazardous impurity of the notified substance, indicating low toxicity to the test species.

EC50	(Daphnia)	> 1000 mg.L ⁻¹ (24h)
LC50	(Zebra Fish)	> 1000 mg.L ⁻¹ (96h)

11. **ASSESSMENT OF ENVIRONMENTAL HAZARD**

The MDI-polyol prepolymer is unlikely to present a hazard to the environment during its use in the production of polyurethane elastomer automotive components.

The notified substance is not expected to exhibit toxic characteristics because large polymers of this nature are not readily absorbed by biota.

Liquid and solid wastes generated from use of the notified substance in the manufacture of the polyurethane elastomer will be treated (to form water insoluble polyureas and polyurethanes) and disposed of, by landfill or incineration, by a Victorian EPA licensed disposal contractor.

12. **ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS**

The product containing the notified chemical also contains 40-80% of MDI. Anticipated health risks associated with the use of this polymer are due to this contaminant. The polymer itself contains 40% low molecular weight species 500 - 1000. Health effects that may occur as a result of exposure to the non MDI monomers component of the prepolymer are unknown.

Free isocyanate is present in quantities of up to 65%. No toxicology data are available on the additive, an isocyanate homopolymer present as 5% of the product. Less than 20% of the reaction product consists of a polymer of number average molecular weight > 1000. This should be considered in determining appropriate precautions.

The product will be used in closed systems for the most part. however occupational exposure may occur during transfer from one vessel to another and during cleaning and maintenance. Vapour pressure is low at room temperature. However, the reaction mixture is transported and stored at elevated temperatures and some operations occur at elevated temperature. Vapours will be generated in these operations and exposure should be prevented.

Exposure to the MDI polyol prepolymer and free isocyanate may cause skin and respiratory irritation and sensitisation, eye irritation and gastrointestinal irritation.

The exposure level and development time for sensitisation to occur are variable, and once sensitisation has occurred the exposure standard will not necessarily be low enough to prevent an allergenic response. Cross sensitisation may occur (8) and, for this reason, workers who are known to have allergic responses such as asthma and hayfever are advised not to work with this or any other MDI containing substance. for those who do handle the chemical, all means must be used to minimise exposure.

Once the new polymer is incorporated into the finished product the risk of exposure is eliminated. However, considerable care must be taken during the transport and storage procedures to avoid a risk to health. Under the proposed conditions of use, public exposure to MDI-polyol prepolymer will be negligible.

13. RECOMMENDATIONS

To minimise exposure to the MDI polyol prepolymer the following guide-lines and precautions should be observed:

- . The MDI polyol prepolymer should be used in closed system equipment.
- . Precautions in the use of MDI polyol prepolymer should recognise the presence of MDI at >50% proportion.

- . Local exhaust ventilation should be used.
- . All precautions should be used to minimise risks, vapours or splashes during transfer of the reaction product between vessels or during maintenance of equipment.
- . Signs to clearly indicate the hazard of the chemical should be clearly posted outside the work areas;
- . The working area must have good general ventilation and exposure standards must be strictly observed.
- . Suitable personal protective equipment should be utilized where exposure to the chemical is possible: safety goggles/shields conforming with Australian Standard (AS)1337-1984 (15); respirators conforming with AS 1715-1991 (16) or AS 1716-1987 (17); gloves conforming with AS 2161-1978 (18); safety boots conforming with AS 2210-1980 (19); overalls conforming with AS 3765.1 (20)
- . Safety shower/eye bath should be located near to the working area.
- . Storage and transport of MDI polyol prepolymer of the must be in accordance with the ADG Code (3).
- . Spills are to be neutralised and mopped up with an inert absorbent such as sawdust and then shovelled into open top containers. These containers should then be removed outside into a well ventilated area and the contents neutralised with 10 parts of a mixture containing 3-8% ammonium hydroxide or 5-10% sodium carbonate in water. The drums are to be left open for 48 hours before being disposed of in an approved landfill or by incineration.

Floors can be decontaminated with water/ammonia solution containing 1-2% detergent which is to be left on the affected area for at least 10 minutes. Brooms etc used during the clean up are to be covered in plastic and disposed of in the manner described above for solid waste.

14. MATERIAL SAFETY DATA SHEET

The Material Safety Data Sheet (MSDS) for MDI polyol prepolymer (Attachment 1) was provided in Worksafe Australia format (21). This MSDS was provided by Dow Chemical Australia Pty Ltd as part of their notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of Dow Chemical Australia Pty Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act), secondary notification of MDI-POLYOL prepolymer shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

16. REFERENCES

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2. RTECS - Registry of Toxic Effects of Chemical Substances. National Institute of Occupational Health and Safety, U.S.
3. Australian Code for the Transport of Dangerous Goods by Road and Rail. Australian Dangerous Goods Code. Fifth Edition. Australian Government Publishing Service, Canberra, September 1992.
4. G Steinhoff and AG Bayer, Institute for toxicology, unpublished studies cited in technical information brochure #4 on monomeric and polymeric MDI, 1982.
5. NIOSH Criteria documents - Diisocyanates, 1978.
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7. D Griffiths-Johnson, K Spear, R Jin, and MH Karol, The Toxicologist 10; Abstract 885, 1990.

8. Chemical Hazard Summary on MDI and PPMDI, Canadian Centre for Occupational Health and Safety, 1987.
9. C Liden, Contact Dermatitis p 301-308
10. Dow Report of Telephone Conservation with Dr Farouk Barbandi, contract physician for Dow Chemical Urethanes Operations LaPorte, Texas 12/19/85
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- 20 Australian Standard 3765.1-1990 Clothing for Protection against Hazardous Chemicals Part 1 Protection against General or Specific Chemicals Standards Association of Australia Publ, Sydney 1990.
- 21 Guidance Note for Completion of a Material Safety Data Sheet. [NOHSC : 3001 (1991)], 3rd Edition, October 1991.