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**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME
(NICNAS)**

FULL PUBLIC REPORT

MDI BASED URETHANE POLYMER P02-243

This Assessment has been compiled in accordance with the provisions of the *Industrial Chemicals (Notification and Assessment) Act 1989* (Cwlth) (the Act) and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by the Department of Health and Ageing, and conducts the risk assessment for public health and occupational health and safety. The assessment of environmental risk is conducted by the Department of Sustainability, Environment, Water, Population and Communities.

For the purposes of subsection 78(1) of the Act, this Full Public Report may be inspected at our NICNAS office by appointment only at Level 7, 260 Elizabeth Street, Surry Hills NSW 2010.

This Full Public Report is also available for viewing and downloading from the NICNAS website or available on request, free of charge, by contacting NICNAS. For requests and enquiries please contact the NICNAS Administration Coordinator at:

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**Director
NICNAS**

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FULL PUBLIC REPORT**MDI BASED URETHANE POLYMER P02-243****1. APPLICANT AND NOTIFICATION DETAILS**

APPLICANT(S)

Dow Chemical (Australia) Ltd (ABN 72 000 264 979)
541-583 Kororoit Creek Road
ALTONA, VIC 3018

NOTIFICATION CATEGORY

Limited: Synthetic polymer with Mn \geq 1000 Da.

EXEMPT INFORMATION (SECTION 75 OF THE ACT)

Data items and details claimed exempt from publication: chemical name, molecular and structural formulae, molecular weight, analytical data, degree of purity, polymer constituents, residual monomers, use details and import volume.

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)

Variation to the schedule of data requirements is claimed as follows: melting/boiling point, density, vapour pressure, water solubility, Log Pow, adsorption/desorption, hydrolysis as a function of pH, flash point, flammability limits, autoignition temperature, explosive properties.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)

CEC/799

NOTIFICATION IN OTHER COUNTRIES

USA 1996

2. IDENTITY OF CHEMICAL

MARKETING NAME(S)

MDI BASED URETHANE POLYMER P02-243 (notified polymer)
BETASEAL FASTFIT (contains < 20% notified polymer)

CAS NUMBER

Not assigned

MOLECULAR WEIGHT

> 10,000 Da

ANALYTICAL DATA

Reference IR and GPC spectra were provided.

3. COMPOSITION

DEGREE OF PURITY > 90%

HAZARDOUS IMPURITIES/RESIDUAL MONOMERS

<i>Chemical Name</i>	Benzene, 1,1'-methylenebis[isocyanato-		
<i>CAS No.</i>	26447-40-5	<i>Weight %</i>	6.9
<i>Hazardous Properties</i>	Conc \geq 25%: Xn; R40; R20; R48/20; R36/37/38; R42/43		
	\geq 10% Conc < 25%: Xn; R40; R48/20; R36/37/38; R42/43		
	\geq 5% Conc < 10%: Xn; R40; R36/37/38; R42/43		
	\geq 1% Conc < 5%: Xn; R40; R42/43		
	\geq 0.1% Conc < 1%: Xn; R42		

NON HAZARDOUS IMPURITIES/RESIDUAL MONOMERS (>1% by weight) None

ADDITIVES/ADJUVANTS None

LOSS OF MONOMERS, OTHER REACTANTS, ADDITIVES, IMPURITIES
Not expected to occur under normal conditions of use.

DEGRADATION PRODUCTS
Not expected to occur under normal conditions of use.

4. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AT 20°C AND 101.3 kPa: Black paste (for the product containing the notified polymer)

Property	Value	Data Source/Justification
Melting Point/Freezing Point	Not determined	The notified polymer will be imported as a component in a paste from which it will not be isolated.
Boiling Point	Not determined	The notified polymer will be imported as a component in a paste from which it will not be isolated.
Density	1,260 kg/m ³	MSDS (for product containing < 20% notified polymer)
Vapour Pressure	< 1.3 × 10 ⁻⁹ kPa	Estimated based on the NAMW > 1,000 Da (US EPA, 2007). The vapour pressure of the residual MDI is 7.2 × 10 ⁻⁷ kPa at 20°C.
Water Solubility	Not determined	Not tested due to the presence of end-groups that readily react with water to form carbon dioxide and insoluble polymeric masses
Hydrolysis as a Function of pH	Not determined	Not tested due to the presence of end-groups that readily react with water to form carbon dioxide and insoluble polymeric masses
Partition Coefficient (n-octanol/water)	Not determined	The notified polymer is expected to react with water and octanol to form carbon dioxide and insoluble polymeric masses
Adsorption/Desorption	Not determined	Not tested due to the presence of end-groups that readily react with water to form carbon dioxide and insoluble polymeric masses
Dissociation Constant	Not determined	The notified polymer has no dissociable functional groups.
Flash Point	> 100°C	MSDS (closed cup, for product containing < 20% notified polymer)
Flammability	Not determined	Expected to be high based on the flash point.
Autoignition Temperature	Not determined	Expected to be high based on the flash point.
Explosive Properties	Not expected to be explosive	The structural formula contains no explosives.

DISCUSSION OF PROPERTIES

Reactivity

The notified polymer contains reactive isocyanate functional groups and will react with atmospheric moisture causing it to crosslink and form a solid.

Dangerous Goods classification

Based on the submitted physical-chemical data in the above table the notified polymer is not classified

according to the Australian Dangerous Goods Code (NTC, 2007). However the data above do not address all Dangerous Goods endpoints. Therefore consideration of all endpoints should be undertaken before a final decision on the Dangerous Goods classification is made by the introducer of the polymer.

5. INTRODUCTION AND USE INFORMATION

MODE OF INTRODUCTION OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS

The notified polymer will not be manufactured or reformulated in Australia. The notified polymer will be imported as a component (< 20%) of a finished sealant product.

MAXIMUM INTRODUCTION VOLUME OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS

<i>Year</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
<i>Tonnes</i>	5-15	5-15	5-15	5-15	5-15

PORT OF ENTRY

Melbourne and Sydney

IDENTITY OF MANUFACTURER/RECIPIENTS

Dow Chemical (Australia) Ltd

TRANSPORTATION AND PACKAGING

The notified polymer will be imported as a prepolymer component of a finished product (sealant) at a concentration of up to 20% in either 600 ml foil sausages or 310 ml cartridges. There will be no local reformulation or repackaging. From the dockside, adhesive material will be off-loaded and transported by road to the notifiers warehouse facilities and then to the designated distributor, or may be sent directly to the end-users ie. auto-glass installation companies.

USE

The notified polymer will be used in a sealant (up to 20% concentration) for automotive windscreen replacement. The sealant will be predominantly used in after-market repair operations.

OPERATION DESCRIPTION

The notified polymer and products containing it will not be manufactured or reformulated within Australia. The notified polymer will be used by automotive repair workers for replacement of windscreen glass. The material will be applied using conventional pumping equipment (i.e. caulking type guns). The cartridge or sausage will be fitted into the caulking gun and the adhesive applied to a localised area around the perimeter of the automotive windshield groove prior to installation of the automotive replacement glass. The total amount of adhesive involved in each application will be typically < 2 kg or < 0.4 kg of notified polymer. The polymer material reacts with atmospheric moisture at the time of application to form an inert solid matrix. Any excess adhesive will be cleaned using a specially formulated cleaning product and a cloth.

6. HUMAN HEALTH IMPLICATIONS

6.1 Exposure assessment

6.1.1 Occupational exposure

NUMBER AND CATEGORY OF WORKERS

<i>Category of Worker</i>	<i>Number</i>	<i>Exposure Duration (hours/day)</i>	<i>Exposure Frequency (days/year)</i>
Transport and warehouse workers	4-8	2	20
Glass replacement workers	100	8	200

EXPOSURE DETAILS

Exposure of transport and storage workers is not expected except in the event of accidental breach of packaging.

As the sealant is applied manually, dermal exposure to the notified polymer is possible during application and manipulation of the automotive windscreen. Inhalation exposure would be limited by the expected low vapour pressure ($< 1.3 \times 10^{-9}$ kPa) of the notified polymer and the low level of low molecular weight species.

Exposure to the notified polymer will be minimised as workers are expected to wear personal protective equipment consisting of impervious overalls, gloves and eye protection goggles. Local exhaust ventilation may be available when general ventilation is inadequate to prevent inhalation exposure to workers.

Once the sealant has cured, the notified polymer becomes bound within a polymer matrix and hence is unavailable for exposure.

6.1.2. Public exposure

The notified polymer is intended for industrial use only; therefore the public may be exposed to the imported product ($< 20\%$ notified polymer) only in the event of a transport accident. The notified polymer will not be available for exposure after the product containing it has been applied to, and becomes an inert part in the frame of automobile windscreens.

6.2. Human health effects assessment

No toxicity data were submitted.

Toxicokinetics, metabolism and distribution.

The notified polymer is not expected to be absorbed across biological membranes, based on the high molecular weight ($> 10,000$ Da) and low percentage of low molecular weight species ($< 1,000$ Da).

Irritation and Sensitisation.

Isocyanates are known to be hazardous to human health. The main hazards posed by isocyanates include respiratory sensitisation in the form of asthma, as well as decreased respiratory function with the possibility of interstitial fibrosis and pulmonary oedema (Tillman, 2007). The UK Employment Medical Advisory Service believes polymeric isocyanate aerosols are capable of causing respiratory sensitisation similar to monomer vapours (ASCC). Isocyanates may also cause respiratory sensitisation by skin contact (US EPA, 2002).

Other adverse health effects of isocyanates may include skin and eye irritation, and skin sensitisation from repeated or prolonged exposure (Kirk-Othmer, 1995). Although the potential for these effects is likely to be reduced due to the high molecular weight of the notified polymer and low percentage of low molecular weight species, these effects cannot be ruled out.

Health hazard classification

Based on the presence of unreacted isocyanate groups, the notified polymer is classified as hazardous according to *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004) with the following risk phrase:

Xn; R42 May cause sensitisation by inhalation.

6.3. Human health risk characterisation

6.3.1. Occupational health and safety

The main route of exposure to the notified polymer ($< 20\%$ concentration) to workers is expected to be dermal exposure, during application of the sealant. Exposure is expected to be limited with the use of personal protective equipment (gloves, protective clothing and safety glasses/goggles). Inhalation exposure to the notified polymer is unlikely, and the notifier has recommended engineering controls such as local exhaust ventilation if vapours containing the notified polymer are generated. Therefore, although the notified polymer is classified as a respiratory sensitiser and a potential eye and skin irritant and skin sensitiser, given the proposed use of PPE and engineering controls, it is not expected to pose an unreasonable health risk to workers.

6.3.2. Public health

The sealant for automotive windscreen replacements, which contains the notified polymer, will only be used by qualified operators. There is no public exposure to the notified polymer, which will be cured and will only be present in inert form in the frame of automobile windscreens.

7. ENVIRONMENTAL IMPLICATIONS

7.1. Environmental Exposure & Fate Assessment

7.1.1 Environmental Exposure

RELEASE OF CHEMICAL AT SITE

The notified polymer will be imported as a component of finished products and further reformulation or repackaging of the notified polymer in Australia is not expected. Accidental spills during transport are expected to be collected, cured and disposed of to landfill.

RELEASE OF CHEMICAL FROM USE

Some notified polymer may be released to the environment as small incidental spills during application (< 5%), or as residues left on the perimeter of the windshield after application (< 5%). A small amount (< 2%) may remain as residue in import containers. These spills and residues will form an inert insoluble polymer matrix on contact with atmospheric moisture. It is anticipated that < 12% of the total imported notified polymer (as a cured insoluble polymer matrix) will be released each year through spills and residues, and these are expected to be collected and disposed of to landfill.

RELEASE OF CHEMICAL FROM DISPOSAL

The majority of the notified polymer will reside on the frame of motor vehicle windcreens after application. At the end of the vehicle's useful life, the glass windcreens and windscreen support frames containing the inert polymer will either be recycled for glass and metal reclamation, or disposed of to landfill.

7.1.2 Environmental fate

No environmental fate data were submitted. The majority of the notified polymer is expected to be disposed of to landfill as cured waste generated during use, residues in empty containers and articles at the end of their useful life. Small quantities of notified polymer in sealant on metal substrates may be sent to metal reclamation facilities. The notified polymer will be irreversibly cross-linked into a solid polymer matrix as part of its normal use pattern and is therefore not expected to be mobile, bioavailable or readily biodegradable. The notified polymer will eventually degrade biotically or abiotically in landfill, or by thermal decomposition during metal reclamation or glass recycling, to generate water and oxides of carbon and nitrogen.

7.1.3 Predicted Environmental Concentration (PEC)

A predicted environmental concentration (PEC) was not determined because the notified polymer is not expected to persist in water due to its hydrolytic instability. Furthermore, the notified polymer is never isolated from sealant products containing the polymer, which reacts with moisture (water) to form insoluble, non-bioavailable, high molecular weight solids. Moreover, very limited aquatic exposure to the notified polymer or its hydrolysis products is expected when the notified polymer is used as proposed.

7.2. Environmental effects assessment

No ecotoxicological data were submitted. The notified polymer is not expected to persist in water due to its hydrolytic instability. Additionally, the notified polymer is never isolated from the sealant, which reacts with moisture (water) to form insoluble, non-bioavailable, high molecular weight solids. Therefore, the notified polymer is not expected to pose a concern to the aquatic environment.

7.2.1 Predicted No-Effect Concentration

The predicted no-effect concentration (PNEC) for the notified polymer has not been calculated as no ecotoxicological data for the polymer were submitted, and as no significant aquatic exposure is expected based on its reported use pattern.

7.3. Environmental risk assessment

The risk quotient ($Q = \text{PEC/PNEC}$) for the notified polymer has not been calculated as release to the aquatic environment is not expected based on its reported use pattern as a component of automotive windscreen sealants. The majority of the notified polymer will be disposed of to landfill as cured sealant. In the cured sealant the notified polymer is irreversibly bound into a solid inert matrix, and is unlikely to be bioavailable or leach in this form. Due to its limited environmental exposure, the risk of the notified polymer to the environment is not expected to be unreasonable based on its reported use pattern.

8. CONCLUSIONS AND REGULATORY OBLIGATIONS

Hazard classification

Based on the presence of unreacted isocyanate groups, the notified polymer is classified as hazardous according to the *Approved Criteria for Classifying Hazardous Substances* [NOHSC:1008(2004)]. The classification and labelling details are:

Xn; R42 May cause sensitisation by inhalation.

and

Due to the lack of toxicological data the classification of the notified polymer using the Globally Harmonised System for the Classification and Labelling of Chemicals (GHS) (United Nations 2003) was not carried out.

Human health risk assessment

Under the conditions of the occupational settings described, the notified polymer is not considered to pose an unreasonable risk to the health of workers.

When used in the proposed manner, the notified polymer is not considered to pose an unreasonable risk to public health.

Environmental risk assessment

On the basis of the reported use pattern, the notified polymer is not considered to pose an unreasonable risk to the environment.

Recommendations

REGULATORY CONTROLS

Hazard Classification and Labelling

- Use the following risk phrases for products/mixtures containing the notified polymer:
 - Conc \geq 1%: R42

Exposure Standard

- A short term exposure limit (STEL) of 0.07 mg/m³ and long term time-weighted-average (TWA) exposure limit of 0.02 mg/m³ applies for the airborne concentration of all isocyanates in the workplace (NOHSC, 1995).

Health Surveillance

- As the notified polymer is a respiratory sensitiser, employers should carry out health surveillance for any worker who has been identified in the workplace risk assessment as having a significant risk of asthma.

CONTROL MEASURES

Occupational Health and Safety

- Employers should implement the following safe work practices to minimise occupational exposure during handling of the notified polymer:
 - Avoid inhalation of vapours, mists and aerosols
 - Avoid contact with skin and eyes
 - Clean spills immediately, taking care to avoid inhalation
- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer as introduced:
 - Organic vapour respirator (as needed)
 - Gloves, overalls and goggles.

Guidance in selection of personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

- A copy of the MSDS should be easily accessible to employees.
- If products and mixtures containing the notified polymer are classified as hazardous to health in accordance with the *Approved Criteria for Classifying Hazardous Substances* [NOHSC:1008(2004)] workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.

Disposal

- The notified polymer should be disposed of to landfill.

Emergency procedures

- Spills or accidental release of the notified polymer should be handled by physical containment, collection and subsequent safe disposal.

Regulatory Obligations

Secondary Notification

This risk assessment is based on the information available at the time of notification. The Director may call for the reassessment of the chemical under secondary notification provisions based on changes in certain circumstances. Under Section 64 of the *Industrial Chemicals (Notification and Assessment) Act (1989)* the notifier, as well as any other importer or manufacturer of the notified chemical, have post-assessment regulatory obligations to notify NICNAS when any of these circumstances change. These obligations apply even when the notified chemical is listed on the Australian Inventory of Chemical Substances (AICS).

Therefore, the Director of NICNAS must be notified in writing within 28 days by the notifier, other importer or manufacturer:

- (1) Under Section 64(1) of the Act; if
 - the polymer has a number-average molecular weight of less than 1000;
 - information has become available to the person on the dermal sensitisation potential of the notified polymer.or
- (2) Under Section 64(2) of the Act; if
 - the function or use of the polymer has changed from a sealant for automotive windscreen replacement, or is likely to change significantly;
 - the amount of polymer being introduced has increased from 15 tonnes, or is likely to increase, significantly;
 - the polymer has begun to be manufactured in Australia;
 - additional information has become available to the person as to an adverse effect of the polymer on occupational health and safety, public health, or the environment.

The Director will then decide whether a reassessment (i.e. a secondary notification and assessment) is required.

Material Safety Data Sheet

The MSDS of a product containing the notified chemical provided by the notifier was reviewed by NICNAS. The accuracy of the information on the MSDS remains the responsibility of the applicant.

BIBLIOGRAPHY

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