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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polymer in Intermediate 170702

This Assessment has been compiled in accordance with the provisions of the *Industrial Chemicals (Notification and Assessment) Act* 1989 (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 National Occupational Health and Safety Commission which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment and the assessment of public health is conducted by the Department of Health and Aged Care.

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Director
Chemicals Notification and Assessment

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1. APPLICANT

Dow Chemical (Australia) Ltd of Kororoit Creek Road, Altona, Victoria 3018 (ABN 72 000 264 979) has submitted a limited notification statement in support of their application for an assessment certificate for Polymer in Intermediate 170702.

2. IDENTITY OF THE CHEMICAL

The chemical name, CAS number, molecular and structural formulae, molecular weight, spectral data, details of the polymer composition and details of exact import volume and customers have been exempted from publication in the Full Public Report and the Summary Report.

Marketing Name: U402 Glass Primer No. 2 U402

3. PHYSICAL AND CHEMICAL PROPERTIES

The following physicochemical data refer to 65–75% notified polymer in methyl ethyl ketone (Intermediate 170702).

Appearance:	Colourless liquid.
Boiling Point:	As for methyl ethyl ketone
Specific Gravity:	1.10
Vapour Pressure:	Not determined. The notified polymer is expected to have a low vapour pressure due to its high molecular weight (NAMW > 1000).
Water Solubility:	20.53 mg/L at 20°C.
Partition Co-efficient (n-octanol/water):	log P_{ow} = 4.05
Hydrolysis as a Function of pH:	Not determined. See comments below.
Adsorption/Desorption:	Not determined. See comments below.

Dissociation Constant:	Not determined. See comments below.
Flash Point:	-3°C, based on the solvent methyl ethyl ketone.
Flammability Limits:	The notified polymer is not expected to be flammable. The product containing the notified polymer is highly flammable due to the methyl ethyl ketone solvent.
Autoignition Temperature:	Not expected to auto-ignite.
Explosive Properties:	Not explosive.
Reactivity/Stability:	Reacts with moisture due to the presence of isocyanate functional groups.

3.1 Comments on Physico-Chemical Properties

Only summary results of the n-octanol and water solubility have been provided with no specific details of the analysis of the notified polymer. The water solubility is given as 20.53 mg/L, which is classed as moderately water-soluble (Mensink *et al* 1995). The solubility in n-octanol is given as >232 g/L.

No test report for determination of the partition coefficient was submitted. The partition coefficient P_{ow} was determined by dividing the n-octanol solubility by the water solubility.

Hydrolysis as a function of pH was not determined. The notified polymer contains carbamate functional groups, which may hydrolyse under extreme temperatures and pH. The polymer also contains terminal isocyanate groups, which react with water.

The adsorption coefficient was not determined. Based on the partition coefficient, the notified polymer is expected to adsorb strongly to organic matter in soil.

The dissociation constant was not determined because the notified polymer does not contain dissociable groups. The –SH groups are weak acids and are expected to have a pKa of 9-11.

4. PURITY OF THE CHEMICAL

Degree of Purity:	Stated as > 98%, however, GPC analysis suggests lower
Hazardous Impurities:	Residual isocyanates
Non-hazardous Impurities (> 1% by weight):	Not identified
Additives/Adjuvants:	Methyl ethyl ketone

5. USE, VOLUME AND FORMULATION

The notified polymer will be imported for use in the automotive glass replacement industry as a component of a fully formulated industrial glass primer at < 20%. The primer will be used as a base for urethane adhesives. The primer will be imported as a viscous liquid in 103 mL and 1 L aluminium bottles and 5 US gallon (19 L) plastic pails in corrugated cardboard or fibreboard boxes. No manufacture or reformulation will occur in Australia.

One tonne of the notified polymer will be imported in the first year, rising to a maximum of 2 tonnes by year 5.

6. OCCUPATIONAL EXPOSURE

Import and Transport

The notified polymer will be transported by road or rail from dockside to a single designated distributor or directly to end use auto-glass installation or OEM companies. No opening of import containers or repackaging of the product containing the notified polymer will occur prior to end-use. Therefore, exposure of approximately 4 - 6 workers involved in import and transport for approximately 1 – 2 hours/day for 10 – 15 days/year will occur only in the event of accidental puncture of the imported bottles or pails.

End-Use: Automotive Glass Installation

At approximately 100 glass replacement workshops, tradesmen working an average of 4 hours/day for 100 days/year will apply the primer using a dauber or small brush directly from the imported containers to the perimeter of automotive windscreen prior to installation. Typically, 15 mL of primer containing the notified polymer at < 20% is applied per application.

As the primer will be applied manually, dermal exposure to the notified polymer is possible during application and manipulation of the automotive windscreen. Although less likely, ocular exposure is possible also from splatter during dauber or brush application of the polymer.

Inhalation exposure to the notified polymer is unlikely due to the high molecular weight and expected low volatility.

Exposure to the polymer will be controlled using local exhaust ventilation in the glass fitting areas. Tradesmen will wear personal protective equipment consisting of impervious overalls, gloves, safety boots and chemical goggles. Worker exposure will be minimised if the primer is applied to motor vehicles at OEM customers using automated robotic equipment.

Once the primer containing the notified polymer cures, the polymer will become bound within a matrix and unavailable for exposure.

7. PUBLIC EXPOSURE

The imported product U402 Urethane Glass Primer No.2 containing the notified polymer will

not be sold to the general public but only used by industry customers. The public may come into contact with the notified polymer only after it has been applied to, and becomes an inert part in automobile glass areas. It is covered by other material and unlikely to be bioavailable.

8. ENVIRONMENTAL EXPOSURE

8.1 Release

Release of the notified polymer to the environment is expected to be minimal because the polymer will not be manufactured or repackaged in Australia, and will be sold directly to customers in the import containers. Release during unloading, storage and transport to the distributor or end user is not anticipated. However, in the event of an accidental spill of the polymer solution into waterways, the polymer is not expected to disperse into the water, but to form a solid precipitate that can be easily collected for disposal.

Most of the notified polymer will be fixed with the glass bonding adhesives to the glass or window frame at the customer sites. The polymer reacts or cures on contact with atmospheric moisture to form an inert solid. Hence, the polymer should remain on the automotive glass until the vehicle or glass reach the end of their lifespan and are disposed of. Some polymer may be released to the environment as small incidental spills during application, or as residues left on the perimeter of the windshield of automobiles after application of the polymer. A small amount may remain as residues in used containers.

The notifier anticipates a total of about 140 kg of the polymer will be released each year through spills and residues. The spills and residues will react with atmospheric moisture to form inert material that is easily collected for disposal. It is expected that the waste polymer will be disposed of in landfill where it may be buried or incinerated.

8.2 Fate

Over 90% of the imported polymer will reside on the perimeter of motor vehicle windscreens after application. At the end of the vehicle's useful life, the glass windscreens and windscreen support frames containing the dried polymer are likely to be either recycled for glass and steel reclamation, or disposed of in landfill. Any residue remaining in containers or scraped from automobiles is also likely to be disposed of in landfill.

Once in contact with moisture the polymer forms a hard, durable solid, which is only slightly soluble in water. Hence any fragments, chips and flakes of the material lost into the environment during application or disposal are expected to be inert.

No biodegradation data were provided in the notification dossier. However, residues disposed of in landfill and entering the soil environment are likely to slowly degrade through abiotic and biotic processes. For example, the notified chemical contains carbamate functional groups, which may eventually hydrolyse, and terminal isocyanate groups, which may react with water helping to break down the substance. Microorganisms in the soil environment are also able to utilise many organic chemicals as an energy source thereby contributing to degradation. Any polymer exposed to sunlight, for example, adhering to glass disposed of at car wreckers, may potentially deteriorate under the action of UV light.

The polymer is not expected to enter the aquatic environment through leaching or runoff in any significant amounts. The partition coefficient indicates the polymer will have an affinity to fat and organic material, hence any dissolved polymer entering the soil environment is expected to adsorb to organic substances.

The high partition coefficient and moderate water solubility indicate a potential to bioaccumulate. However, the polymer has a relatively high average molecular weight (> 1000) and a low percentage of components with MW below 500, and hence is not expected to diffuse across biological membrane and bioaccumulate (Walker 2001).

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Summary of Toxicological Investigations

A single summary of a rat acute oral toxicity study was submitted for Intermediate 170702 containing 65 – 75% notified polymer.

Endpoint & Result	*Assessment Conclusion*
Rat, acute oral LD_{50} > 2000 mg/kg bw	low toxicity

9.1.1 Acute Oral Toxicity (Dow Chemical Company, 1999b)

TEST SUBSTANCE	Intermediate 170702 (65 – 75% notified polymer).
METHOD	Internal Dow Chemical Test Procedure – similar to OECD TG 401
Species/Strain	Rat/ Fisher 344
Vehicle	None

RESULTS

Group	*Number & Sex of Animals*	*Dose mg/kg bw*	*Mortality*
1	3	2000	None

LD50	> 2000 mg/kg bw
Signs of Toxicity	All rats gained weight and no clinical signs of toxicity were noted during the study.
Effects in Organs	No comments were recorded in the study summary.
CONCLUSION	The notified chemical is of low toxicity via the oral route.
TEST FACILITY	Health and Environmental Sciences, Dow Chemical Company, Michigan, USA.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

The notifier has provided a test report for the acute toxicity to fish test. The test was carried

out according the guidelines and protocols of US EPA Toxic Substances Control Act. The test results are shown in the table below.

Test	*Species*	*Results*
Acute Toxicity to Fish (US EPA TG 797.1400)	Rainbow Trout *Oncorhynchus mykiss*	72 and 96 h LC_{50} = 1.55 mg/L 48 h LC_{50} = 1.85 mg/L 24 h LC_{50} = 1.96 mg/L 96 h NOEC < 0.625 mg/L

* NOEC - no observable effect concentration

A definitive Toxicity to Fish Test of Intermediate 170702 was conducted over a 96 hour period against 20 rainbow trout per dose level (2 replicates per concentration; 10 fish per replicate) using nominal concentrations of 0.625, 1.25, 2.5, 5.0, and 10 mg/L of the test substance. Test solutions were prepared using serial dilutions of a 133 mg/L concentrated stock solution (Dow Chemical Company, 1999a).

Because the test material was insoluble in water, a primary stock solution was prepared by dissolving the test substance in acetone, and then making up the required concentrations from the primary stock solution. Control test vessels were also set up containing only dilution water and acetone. At the highest dose (10 mg/L), the test material precipitated out of solution, forming crystals on the sides and bottom of the test vessel, and forming a thin film on top of the water surface. Precipitation was not observed at lower dose levels.

All of the fish exposed to concentrations of 5 and 10 mg/L of test substance had died after 24 hours. 85% of fish exposed to concentrations of 2.5 mg/L of test substance had died after 24 hours, and 90% were dead after 48 hours. The mortality of fish exposed to concentrations of 1.25 mg/L of the substance was 0% after 48 hours, and 15% after 72 and 96 hours. The mortality of fish exposed to concentrations of 0.625 mg/L of the substance was 0% after 24 hours, 5% after 48 hours, and 10% after 72 and 96 hours.

Sublethal effects observed throughout the course of the study were hemorrhaging in the region of the head including the snout, opercule, maxilla, and mandible areas; dark pigmentation of the skin; lethargy; loss of equilibrium and swimming at the surface. Hemorrhaging was seen in 28%, and skin pigmentation in 22%, of the surviving fish exposed for 24 hours, and was seen at concentrations as low as 0.625 mg/L. On the basis of the sublethal effects observed during the study, the 24-, 48-, 72, and 96- hour EC_{50} concentrations of Intermediate 170702, were 1.04, 1.35, 1.58, and 1.58 mg/L respectively.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The results of the toxicity test indicate that the new polymer is toxic to fish, having adverse effects on fish at concentrations above 0.625 mg/L. While no toxicity tests for other aquatic organisms were provided in the dossier, it is likely that the substance is toxic to other aquatic and terrestrial organisms as well. The new polymer contains carbamate functional groups. Carbamates are inherently toxic and are the active functional groups in many commonly used pesticide compounds (Manahan, 1993).

Despite the polymer's potential toxicity to organisms, because of the usage patterns and physical properties of the polymer, it is not expected to pose a hazard to the environment. The

polymer will not be manufactured or repackaged in Australia. It will be applied in small quantities in closed workshops, and once applied, will become fixed to glass. The polymer contains functional groups allowing the material to form an inert, insoluble compound when in comes into contact with atmospheric moisture. Hence, there will be little opportunity for the polymer to enter the aquatic environment and for aquatic organisms to become exposed to the polymer. In the event that the polymer does enter waterways, it would be expected to enter sewage treatment facilities from where it would be removed with solid waste sludge.

The new polymer is not expected to pose a hazard to organisms in the soil environment at landfill sites. The waste polymer disposed of directly to landfill will be in an inert form, and will be disposed of in small quantities, owing to the anticipated small release volumes and the nationwide use.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Hazard assessment

A summary of a rat acute oral toxicity study was provided for Intermediate 170702 containing 65-75% notified polymer. The study summary indicates that this product was of low acute oral toxicity in rats. No other toxicological data were provided.

Because only limited toxicological information has been provided for the notified polymer, the polymer has not been classified against the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999). Despite a high molecular weight (> 1000) which would suggest a low bioavailability, the notified polymer contains isocyanate functional groups which in lower molecular weight species may possess toxicological impact. Accordingly, the MSDS for Intermediate 170702 carries a hazard classification with warnings of respiratory sensitisation due to isocyanates. The MSDS also carries warnings of skin and eye irritation and central nervous system depression due to the presence of methyl ethyl ketone solvent. Similar warnings are also carried on the MSDS for the imported hazardous U402 Urethane Glass Primer No.2 product containing < 20% notified polymer.

Intermediate 170702 and the imported U402 Urethane Glass Primer No.2 are classified as Class 3 Dangerous Goods due to the presence of solvent.

Occupational health and safety

Bottles and pails of product containing the notified polymer will not be opened prior to end-use and so for import and transport workers, exposure to the notified polymer is likely to occur only as a result of an accident. Therefore, the notified polymer represents a low health risk for these workers.

The notified polymer is used in a primer applied to the windscreen frames of motor vehicles prior to installation of the glass. Dermal and to a lesser extent ocular exposure to the notified polymer may occur when applying primer to the glass and when removing residues. Inhalation exposure to the notified polymer will be limited by local exhaust ventilation in the glass replacement workshops. The ventilation is necessary also to minimise exposure to the hazardous solvents present in the primer. If exposure to the notified polymer occurs, irritation may result. Given the possibility of residual isocyanates present in the primer, allergic

sensitisation may occur also with prolonged or frequent exposure. Therefore, dermal and ocular exposure should be controlled by personal protective equipment consisting of impervious overalls and safety boots, gloves and chemical goggles. If the glass replacement process is automated, for example, by use of robotic equipment, then the risk of adverse health effects from the notified polymer and other hazardous components of the imported primer will be substantially reduced.

As the notified polymer reacts with atmospheric moisture to form an inert solid mass, contact with the polymer after application is of low risk.

Public health

The imported product containing the notified polymer will not be sold to the general public, and only be used by industry customers. The public may come into contact with the notified polymer only after it has been applied to, and becomes an inert part in automobile glass areas. It is covered by other material and unlikely to be bioavailable. Therefore, the potential risk of the notified polymer to public health is considered to be low.

13. RECOMMENDATIONS

Control Measures

Occupational Health and Safety

- Employers should implement the following engineering controls to minimise occupational exposure to the notified polymer as introduced:

  - Local exhaust ventilation should be fitted to glass fitting areas

- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer as introduced:

  - Impervious coveralls and footwear
  - Impervious gloves
  - Chemical 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 NOHSC *Approved Criteria for Classifying Hazardous Substances*, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.

Storage

- The following precautions should be taken regarding storage of the notified chemical:

– Storage at 10-35°C indoors in tightly closed containers due to reactivity with moisture.

Secondary Notification

The Director of Chemicals Notification and Assessment must be notified in writing within 28 days by the notifier, other importer or manufacturer:

(1) Under Subsection 64(1) of the Act; if
– If the polymer is imported as Intermediate 170702

or

(2) Under Subsection 64(2) of the Act:
- if any of the circumstances listed in the subsection arise.

The Director will then decide whether secondary notification is required.

No additional secondary notification conditions are stipulated.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the notified chemical was provided in a format consistent with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (National Occupational Health and Safety Commission, 1994).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

15. REFERENCES

Dow Chemical Company (1999a) Aquatic Screening of the [Intermediate 170702] in the Rainbow Trout, *Oncorhynchus mykiss* Walbaum. Study ID: 990021, 18 February 1999. Toxicology Research Laboratory, The Dow Chemical Company, Midland, Michigan, USA. (Unpublished report provided by Dow Chemical Australia Ltd).

Dow Chemical Company (1999b) [Intermediate 170702]: Acute oral toxicity study in F344 rats. Study ID: 980391, 16 February 1999. Health and Environmental Research Laboratories, The Dow Chemical Company, Midland, Michigan, USA. (Unpublished report provided by Dow Chemical Australia Ltd).

Manahan SE (1993) Fundamentals of Environmental Chemistry. Lewis Publishers. Michigan, USA.

Mensink BJWG, Monforts M, Wijkuizen-Maslankiewicz, L, Tibosch H and Linders JBHJ (1995) Manual for summarising and evaluating the environmental aspects of pesticides,

National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands. Report no. 679101022.

National Occupational Health and Safety Commission (1994) National Code of Practice for the Preparation of Material Safety Data Sheets [NOHSC:2011(1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1999) Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(1994)]. Australian Government Publishing Service, Canberra.

Walker CH (2001) Organic Pollutants an Ecotoxicological Perspective. Taylor & Francis, London and New York.

Attachment 1

The Draize Scale (Draize, 1959) for evaluation of skin reactions is as follows:

Erythema Formation	*Rating*	*Oedema Formation*	*Rating*
No erythema	0	No oedema	0
Very slight erythema (barely perceptible)	1	Very slight oedema (barely perceptible)	1
Well-defined erythema	2	Slight oedema (edges of area well-defined by definite raising	2
Moderate to severe erythema	3	Moderate oedema (raised approx. 1 mm)	3
Severe erythema (beet redness)	4	Severe oedema (raised more than 1 mm and extending beyond area of exposure)	4

The Draize scale (Draize *et al*., 1944) for evaluation of eye reactions is as follows:

CORNEA

Opacity	*Rating*	*Area of Cornea involved*	*Rating*
No opacity	0 none	25% or less (not zero)	1
Diffuse area, details of iris clearly visible	1 slight	25% to 50%	2
Easily visible translucent areas, details of iris slightly obscure	2 mild	50% to 75%	3
Opalescent areas, no details of iris visible, size of pupil barely discernible	3 moderate	Greater than 75%	4
Opaque, iris invisible	4 severe		

CONJUNCTIVAE

Redness	*Rating*	*Chemosis*	*Rating*	*Discharge*	*Rating*
Vessels normal	0 none	No swelling	0 none	No discharge	0 none
Vessels definitely injected above normal	1 slight	Any swelling above normal	1 slight	Any amount different from normal	1 slight
More diffuse, deeper crimson red with individual vessels not easily discernible	2 mod.	Obvious swelling with partial eversion of lids	2 mild	Discharge with moistening of lids and adjacent hairs	2 mod.
Diffuse beefy red	3 severe	Swelling with lids half-closed	3 mod.	Discharge with moistening of lids and hairs and considerable area around eye	3 severe
		Swelling with lids half-closed to completely closed	4 severe		

IRIS

Values	*Rating*
Normal	0 none
Folds above normal, congestion, swelling, circumcorneal injection, iris reacts to light	1 slight
No reaction to light, haemorrhage, gross destruction	2 severe

Draize, J. H., Woodward, G., Calvery, H. O. (1944) Methods for the Study of Irritation and Toxicity of Substances Applied Topically to the Skin and Mucous Membranes, J. Pharmacol. Exp. Ther. 82 : 377-390.

Draize J. H. (1959) Appraisal of the Safety of Chemicals in Foods, Drugs and Cosmetics. Association of Food and Drug Officials of the US, 49 : 2-56.