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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

PUBLIC REPORT

Polymer in Betaprime 5500 and 5504G

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 Public Report may be inspected at our NICNAS office by appointment only at Level 7, 260 Elizabeth Street, Surry Hills NSW 2010.

This 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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SUMMARY

The following details will be published in the NICNAS Chemical Gazette:

ASSESSMENT REFERENCE	APPLICANT(S)	CHEMICAL OR TRADE NAME	HAZARDOUS CHEMICAL	INTRODUCTION VOLUME	USE
LTD/1618	Dow Chemical (Australia) Ltd	Polymer in Betaprime 5500 and 5504G	Yes	< 20 tonnes per annum	Component of primers for automotive windscreens

CONCLUSIONS AND REGULATORY OBLIGATIONS

Hazard classification

As no toxicity data were provided, the notified polymer cannot be classified according to the *Globally Harmonised System for the Classification and Labelling of Chemicals* (GHS), as adopted for industrial chemicals in Australia.

Based on the presence of the isocyanate functional group in the notified polymer, the notified polymer is recommended for hazard classification according to the *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004) with the following risk phrase:

R42: May cause sensitisation by inhalation

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 its expected low hazard and assessed use pattern, the notified polymer is not considered to pose an unreasonable risk to the environment.

Recommendations

REGULATORY CONTROLS

Health Surveillance

 As the notified polymer contains isocyanate functional groups, employers should carry out health surveillance for any worker who has been identified in the workplace risk assessment as having a history of isocyanate sensitivity, asthma or other pulmonary condition and who may be adversely affected by isocyanate exposure.

CONTROL MEASURES

Occupational Health and Safety

- Employers should implement the following engineering controls to minimise occupational exposure to the notified polymer during use:
 - Good general ventilation including local exhaust ventilation if necessary.
- Employers should implement the following safe work practices to minimise occupational exposure during handling of the products containing the notified polymer:
 - Avoid inhalation of vapours, mists and aerosols
 - Avoid contact with skin and eyes

 Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer during use of products containing the notified polymer:

- Isocyanate-resistant gloves
- Coveralls
- Safety glasses
- Appropriate respiratory protection where inhalation exposure may occur

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

- Atmospheric monitoring should be conducted to measure workplace concentrations of isocyanates during use of products containing the notified polymer. Employers should ensure that the exposure standard for isocyanates [NOHSC: 1003(1995)] is not exceeded for all areas where the notified polymer will be handled.
- A copy of the (M)SDS should be easily accessible to employees.
- If products and mixtures containing the notified polymer are classified as hazardous to health in accordance with the *Globally Harmonised System for the Classification and Labelling of Chemicals (GHS)* as adopted for industrial chemicals in Australia, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation should 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 polymer 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;
- (2) Under Section 64(2) of the Act; if
 - the function or use of the polymer has changed from a component of primers for automotive windscreens, or is likely to change significantly;
 - the amount of polymer being introduced has increased from 20 tonnes per annum, 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 (M)SDS of products containing the notified polymer provided by the notifier were reviewed by NICNAS. The accuracy of the information on the (M)SDS remains the responsibility of the applicant.

ASSESSMENT DETAILS

1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)
Dow Chemical (Australia) Limited (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, other names, molecular and structural formulae, molecular weight, degree of purity, polymer constituents, residual monomers, and import volume.

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)

Variation to the schedule of data requirements is claimed for all physico-chemical properties.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S) CEC/809

NOTIFICATION IN OTHER COUNTRIES

None

2. IDENTITY OF CHEMICAL

MARKETING NAME(S)

Betaprime 5500 (contains the notified polymer at < 40% concentration)

Betaprime 5504G (contains the notified polymer at < 40% concentration)

MOLECULAR WEIGHT

Mn Value >1,000 Da

ANALYTICAL DATA

Reference IR and GPC spectra were provided.

3. COMPOSITION

DEGREE OF PURITY > 95%

4. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AT 20 °C AND 101.3 kPa: Black liquid (for product containing < 40% notified polymer)

Property	Value	Data Source/Justification
Melting Point/Freezing Point	Not determined	Introduced as a solvent solution.
Boiling Point	Not determined	Introduced as a solvent solution.
Density	950 kg/m^3	M)SDS (for product containing < 40% notified polymer).
Vapour Pressure	$< 1.3 \text{ x } 10^{-9} \text{ kPa at } 25 \text{ °C}$	Estimated based on the NAMW > 1000 Da (US EPA, 2010)
Water Solubility	Not determined	Not determined due to the presence of

		end-groups that readily react with water to form carbon dioxide and insoluble high molecular weight	
Hydrolysis as a Function of pH	Reacts with water	polymers. Measured. Contains functionality that is expected to rapidly hydrolyse in	
Partition Coefficient (n-octanol/water)	Not determined	water. The notified polymer is hydrolytically unstable and a meaningful partition coefficient cannot be determined	
Adsorption/Desorption	Not determined	Not tested due to hydrolytic instability. Likely to adsorb to sludge, soil and sediment based on its high molecular weight.	
Dissociation Constant	Not determined	No dissociable groups present.	
Particle Size	Not determined	Introduced as a solvent solution.	
Flash Point	Not determined	Not expected to form flammable vapours based on NAMW > 1000 Da.	
Flammability	Not determined	Imported in flammable product.	
Autoignition Temperature	Not determined	Not expected to autoignite.	
Explosive Properties	Not expected to be explosive	Contains no functional groups that would imply explosive properties.	
Oxidising Properties	Not expected to be oxidising	Contains no functional groups that would imply oxidising properties.	

DISCUSSION OF PROPERTIES

Reactivity

The notified polymer contains reactive end groups that react with moisture causing the polymer to cross-link and form a solid mass, and release the toxic and flammable vapour (methanol).

Physical hazard classification

Based on the submitted physico-chemical data depicted in the above table, the notified polymer is not recommended for hazard classification according to the *Globally Harmonised System for the Classification and Labelling of Chemicals (GHS)*, as adopted for industrial chemicals in Australia.

5. INTRODUCTION AND USE INFORMATION

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

The notified polymer will be imported as a component (< 40%) of a finished solvent based primer product.

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

Year	1	2	3	4	5
Tonnes	< 20	< 20	< 20	< 20	< 20

PORT OF ENTRY

Melbourne and Sydney.

TRANSPORTATION AND PACKAGING

The notified polymer will be imported as a component of a finished product at a concentration of up to 40% concentration in aluminium bottles of up to 1L. The aluminium bottles will be transported by road to the notifiers warehouse facilities and then to the designated distributor, or may be sent directly to the end-users i.e. auto-glass installation companies.

Use

The notified polymer will be used as a component of primers for the replacement of automotive windscreen glass.

OPERATION DESCRIPTION

The notified polymer and products containing it will not be manufactured or reformulated within Australia. Primers containing the notified polymer at < 40% concentration will be used by trained automotive repair workers for

replacement of automotive windscreen glass. The primer will be applied using a woollen dauber (similar to a cotton bud on a wire handle) or through use of a specialised application bottle. Windscreen repair workers will open the 1 L containers and will insert the applicator (woollen dauber or manually decant the required volume into the application bottle). The primer will then be applied to a localised area around the perimeter of the automotive windshield groove prior to the application of the adhesive/sealant and installation of the automotive replacement glass. Any excess primer will be cleaned using a speciality formulated cleaning product and a cloth. The notified polymer material reacts with atmospheric moisture at the time of application to form an inert solid matrix.

6. HUMAN HEALTH IMPLICATIONS

6.1. Exposure Assessment

6.1.1. Occupational Exposure

CATEGORY OF WORKERS

Category of Worker	Exposure Duration (hours/dav)	Exposure Frequency (days/year)
Transport and warehouse workers	2	20
Glass replacement workers	8	200

EXPOSURE DETAILS

Transport and storage

Transport and storage workers may come into contact with the imported product containing the notified polymer at up to 40% concentration, only in the unlikely event of an accident.

End use

Dermal exposure to the notified polymer at concentrations up to 40% may occur during application of the primer products containing the notified polymer to windscreens. There is also potential for inhalation exposure given the relatively high percentage of low molecular weight species.

Workers may also be exposed to the toxic and flammable vapour (methanol) that is released during curing of the primer containing the notified polymer.

Exposure to the notified polymer will be minimised by the use of safety glasses, impervious gloves and coveralls. Typically, the windscreen repair operation is carried out in an outdoor area or within an automotive repair workshop which is a large area with good natural ventilation. However, local exhaust ventilation or mechanical ventilation may be used where general ventilation is inadequate to prevent inhalation exposure to workers.

Once the primers are cured and dried, the notified polymer becomes bound within a polymer matrix and will be unavailable for exposure.

6.1.2. Public Exposure

The notified polymer is intended for industrial use only. The public may come into contact with the cured primer containing the notified polymer. However, once cured and dried, the notified polymer becomes bound within a polymer matrix and will be unavailable for exposure.

6.2. Human Health Effects Assessment

No toxicity data were submitted for the notified polymer.

The notified polymer is not expected to be absorbed across biological membranes to a significant extent, based on its high molecular weight (Mn > 1000 Da). However, the polymer contains a relatively high percentage of low molecular weight species (< 1000 Da) that may be absorbed.

The notified polymer contains isocyanate functional groups that are of concern for irritation, dermal and respiratory sensitisation and pulmonary toxicity (Barratt, 1994; USEPA, 2010; Kirk-Othmer 1995).

The USEPA specifies that structures with isocyanate equivalent weights of $\geq 5,000$ are presumed not to pose a hazard under any conditions. In addition, concerns are generally confined to species with molecular weights \leq

1,000. The isocyanate functional group equivalent weight of the notified polymer is < 5,000 and although its molecular weight is > 1,000, the polymer contains a relatively high proportion of low molecular weight species, hence the risks cannot be ruled out.

Polymeric isocyanates tend to be non-volatile and are therefore expected to be less of an inhalation hazard compared to non-polymeric isocyanates. However, polymeric isocyanate aerosols may cause respiratory sensitisation similar to monomer vapours, and reports have shown that inhalation of relatively non-volatile isocyanates in the form of dusts and spray-mists could cause adverse respiratory effects (HSIS, 2008). Isocyanates may also cause respiratory sensitisation by skin contact (US EPA, 2010).

According to the *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004), substances containing isocyanate functional groups should be classified as hazardous if there is no evidence to indicate that the substance does not cause respiratory hypersensitivity. Thus, the following risk phrase should be applied to the notified polymer:

R42: May cause sensitisation by inhalation.

The notified polymer also contains alkoxysilyl functional groups that are a concern for systemic toxicity and skin irritation. The systemic concerns in particular relate to lung toxicity from vapours or aerosols and are based on data from low molecular weight molecules (USEPA, 2010). The potential for these effects may be limited by the high molecular weight of the notified polymer but cannot be ruled out given the high proportion of low molecular weight species.

The notified polymer also releases a toxic and flammable vapour (methanol) during curing.

Health hazard classification

As no toxicity data were provided, the notified polymer cannot be classified according to the *Globally Harmonised System for the Classification and Labelling of Chemicals (GHS)*, as adopted for industrial chemicals in Australia.

Based on the presence of the isocyanate functional group in the notified polymer, the notified polymer is recommended for hazard classification according to the *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004) with the following risk phrase:

R42: May cause sensitisation by inhalation.

6.3. Human Health Risk Characterisation

6.3.1. Occupational Health and Safety

No toxicological data were supplied for the notified polymer. On the basis of the presence of isocyanate and alkoxysilane functional groups and relatively high proportion of low molecular weight species, the notified polymer may cause irritation, dermal and respiratory sensitisation and systemic toxicity. The notified polymer also releases a toxic and flammable vapour (methanol) during curing.

During application of the primer products containing the notified polymer, there is potential for inhalation and dermal exposure to the notified polymer at concentrations of < 40%. In addition, there is potential for inhalation exposure to methanol released from the notified polymer during curing of the primer containing the notified polymer. However, exposure of workers to the notified polymer and the toxic vapour methanol is expected to be low due to the control measures in place (i.e the use of PPE, including respiratory protection where appropriate, and the conducting of glass-fitting in well-ventilated areas) to minimise exposure to the hazardous substances (i.e. low molecular weight isocyanates) in the primer products containing the notified polymer.

Given the control measures in place to minimise exposure involved in handling the hazardous substances present in the primer products containing the notified polymer, the risk to workers due to exposure to the notified polymer is not considered to be unreasonable.

6.3.2. Public Health

The primer products for automotive windscreen replacements, which contain the notified polymer, will only be used by qualified workers. There is no expected public exposure to the notified polymer, which will be cured and will only be present in inert form in the frame of automobile windscreens. As such, the risk to the public

from the use of the notified polymer is not considered to be unreasonable.

7. ENVIRONMENTAL IMPLICATIONS

7.1. Environmental Exposure & Fate Assessment

7.1.1. Environmental Exposure

RELEASE OF CHEMICAL AT SITE

The notified polymer is not manufactured or reformulated in Australia; therefore, there will be no release from these activities. In the event of an accidental spill during transport, distribution or storage, the notified polymer is expected to cure in the presence of atmospheric moisture to form a solid mass. These wastes are expected to be collected and disposed of in accordance with local regulations.

RELEASE OF CHEMICAL FROM USE

The primer products containing the notified polymer will be used by industrial end users. Therefore, following application of the notified polymer, any residual inert material around the perimeter of the windshield will be cleaned off using a solvent formulation and a cloth or, if cured, cut-off and disposed of via existing solid waste streams for adhesive products. Cleaning cloths are expected to be disposed of to landfill. Any residual notified polymer in application bottles, estimated to be 2% of total import volume, will react with atmospheric moisture to form an inert material and is expected to be disposed of to landfill.

RELEASE OF CHEMICAL FROM DISPOSAL

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

7.1.2. Environmental Fate

No environmental fate data were submitted. The mixture containing the notified polymer reacts or cures on contact with atmospheric moisture to form an inert solid. Most of the notified polymer is expected to be disposed of to landfill as cured solids adhering to articles, as residues in empty containers or in waste generated during use. The notified polymer will be irreversibly cross-linked to form an inert polymeric matrix as part of its reported use pattern. In this form it is not expected to be mobile, bioavailable or readily biodegradable. Small quantities of notified polymer may be thermally decomposed during metals reclamation or glass recycling. The notified polymer will eventually degrade in landfill, or by thermal decomposition during metal reclamation or glass recycling, to generate water and oxides of carbon, silicon 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 the aquatic compartment due to its hydrolytic instability. Further, the notified polymer is never isolated from primer products containing the polymer, which rapidly 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 primer products, which reacts with moisture (water) to form insoluble, non-bioavailable, high molecular weight solids. Therefore, the notified polymer is expected to be of low 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 the notified polymer is expected to be of low concern to the aquatic environment.

7.3. Environmental Risk Assessment

The risk quotient (Q = 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 primers. The majority of the notified polymer will be disposed of to landfill as inert cured solids. The notified polymer is irreversibly bound in an inert matrix, and is unlikely to be bioavailable or mobile in this form. Therefore, based on its expected low hazard and assessed use pattern, the notified polymer is not considered to pose an unreasonable risk to the environment.

APPENDIX A: PHYSICAL AND CHEMICAL PROPERTIES

Hydrolysis as a Function of pH

Method Similar to OECD TG 111 Hydrolysis as a Function of pH.

Remarks The stability of the notified polymer was determined over 2 weeks at 40°C in aqueous buffers with pH 4, 7 and 9 and 1 day at 40°C in an aqueous buffer with pH 1.2. The

concentration of the notified polymer in the test solutions was 4000 mg/L.

There were no significant changes in the FR-IR spectra or Py-GC-MS pattern of notified polymer isolated from the test solutions. However, the solid component in each test solution was insoluble in the GPC solvent and thus the change in the molecular weight of the notified polymer could not be determined. The insolubility of the notified polymer in the GPC solvent is likely to be due to the reaction between the notified polymer and moisture, and subsequent cross-linking, to form insoluble high molecular weight masses.

Test Facility KOPTRI (2011)

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