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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

FULL PUBLIC REPORT

Polymer in Polyamine 1420/46

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 the Environment, Water, Heritage and the Arts.

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 334-336 Illawarra Road, Marrickville NSW 2204.

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:

Street Address: 334 - 336 Illawarra Road MARRICKVILLE NSW 2204, AUSTRALIA.

Postal Address: GPO Box 58, SYDNEY NSW 2001, AUSTRALIA.

TEL: + 61 2 8577 8800 FAX + 61 2 8577 8888 Website: www.nicnas.gov.au

Director NICNAS

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FULL PUBLIC REPORT

Polymer in Polyamine 1420/46

1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)

The Trustee for Endeavour Chemicals and Plastics Trust (ABN 31 383 329 179) 6/423 King Georges Road BEVERLEY HILLS NSW 2209

NOTIFICATION CATEGORY

Limited: Synthetic polymer with $Mn \ge 1000 Da$.

EXEMPT INFORMATION (SECTION 75 OF THE ACT)

Data items and details claimed exempt from publication:

Chemical name; Molecular formula; Structural formula; Molecular weight; Spectral data; Methods of detection and determination; Import volume; Confidential details of use; Residual Monomers; Polymer Constituents; Identity of manufacturer and recipients.

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)

Variation to the schedule of data requirements is claimed as follows:

Melting point, Boiling point, Vapour pressure, Hydrolysis as a function of pH, Partition coefficient, Particle size, Adsorption/Desorption, Dissociation constant, Flammability, Autoignition temperature, Explosive properties

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)

No

NOTIFICATION IN OTHER COUNTRIES

None

2. IDENTITY OF CHEMICAL

MARKETING NAME(S) Polyamine 1420/46

MOLECULAR WEIGHT

Mn > 1000 Da % of Low MW species < 1000 Da > 25%

ANALYTICAL DATA

Reference IR and GPC spectra were provided.

3. COMPOSITION

DEGREE OF PURITY 68%

HAZARDOUS IMPURITIES/RESIDUAL MONOMERS

Chemical Name *Cyclohexanemethanamine, 5-amino-1,3,3-trimethyl (IDPA)

CAS No. 2855-13-2 Weight % 25-30

Hazardous Properties Xn; R21/22 C; R34 R43 R52-53

Conc ≥ 25%: C; R34; R21/22; R43 ≥ 10%Conc < 25%: C; R34; R43 ≥ 5%Conc < 10%: Xi; R36/38; R43

≥ 1%Conc < 5%: Xi; R43

NON HAZARDOUS IMPURITIES/RESIDUAL MONOMERS (>1% by weight)

None

ADDITIVES/ADJUVANTS None

4. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AT 20°C AND 101.3 kPa:

Slightly yellow aqueous solution (for Polyamine 1420/46 containing ~55% notified polymer)

Property	Value	Data Source/Justification
Melting point	Not determined	Will only be imported as an aqueous
		solution.
Density	$1020 \text{ kg/m}^3 \text{ at } 20^{\circ}\text{C}^1$	MSDS
Vapour Pressure	$< 2 \times 10^{-3} \text{ kPa}^2$	Estimated based on vapour pressure for
		IDPA.
Water Solubility	Not determined	Expected to be slightly soluble (see
		discussion below for more details).
Hydrolysis as a Function of pH	Not determined	No hydrolysable functional groups.
Partition Coefficient	Not determined	Expected to be relatively low based on
(n-octanol/water)		water solubility.
Adsorption/Desorption	Not determined	Expected to be associated with soil and
1		sediment based on low water solubility.
Dissociation Constant	Not determined	Contains basic functionalities with a pka
		of 10-11.
Particle Size	Not determined	Not isolated from aqueous solution.
Flash Point	> 100°C at 101.3 kPa ¹	MSDS. Not isolated from aqueous
		solution.
Flammability	Not determined	Not isolated from aqueous solution.
Autoignition Temperature	Not determined	Not expected to autoignite under normal
		conditions of use.
Explosive Properties	Not expected to be explosive	The structural formula contains no
		explosophores.

¹ For Polyamine 1420/46 (~55% notified polymer)

^{*} Monomer used in manufacture of notified polymer

² For 5-amino-1,3,3-trimethyl-cyclohexanemethanamine (IPDA)

DISCUSSION OF PROPERTIES

The notified polymer is expected to have a low vapour pressure, limited water solubility and to be slightly lipophilic. Expected to be protonated in the environmental pH range of 4-9.

Water solubility

The notifier reports that Polyamine 1420/46 (~55% notified polymer) is miscible with up to 52% water, and that upon addition of more water to the mixture i.e. > 52%, phase separation results. This result at first seems unusual at it implies that the notified polymer becomes less soluble upon dilution with water. Based on the structure and the Mn of > 1000 Da, the notified polymer would be expected to have limited water solubility. This unusual water solubility can be explained by the high percentage of residual monomer that is highly water-soluble and aids in keeping the notified polymer in solution upon addition of water up to 52% w/w.

The phase-separated material that is surmised to be largely the notified polymer was isolated and added to additional water, however no measurable water solubility occurred. Although this result would suggest that the notified polymer is not soluble in water, it is noted that the notified polymer has a high polydispersity and a high percentage of low molecular weight species < 1000 Da. It is likely that some components of the notified polymer will have some degree of water solubility.

Reactivity

The notified polymer is expected to be stable under normal storage and handling conditions.

Dangerous Goods classification

Based on the available data the notified polymer is classified as follows according to the Australian Dangerous Goods Code (FORS, 1998):

Class 8 (Corrosive)

5. INTRODUCTION AND USE INFORMATION

MODE OF INTRODUCTION OF NOTIFIED CHEMICAL (100%) OVER NEXT 5 YEARS The notified polymer will be imported by sea or air as an aqueous solution (~55% w/w).

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

Year	1	2	3	4	5
Tonnes	3-10	10-30	30-100	100-300	100-300

PORT OF ENTRY

Sydney, Melbourne and Brisbane.

TRANSPORTATION AND PACKAGING

The notified polymer (~55% w/w aqueous solution) will be transported from the sea and airports by road to paint formulators in 180 to 250 kg plastic drums.

The formulated coating products (< 10% notified polymer) will be packaged in 1, 3, 5, 10 and 20 L rigid thick-walled HDPE drums and transported by road to customer sites.

USE

The notified polymer will be used as a hardener for epoxy resins in surface coatings for industrial applications.

OPERATION DESCRIPTION

Formulation

The notified polymer (\sim 55% w/w) will be transferred from the imported drums to open or closed mixing vessels either by manual addition or through an automated process. After the addition of additives, pigments and co-solvents, the finish coating products (< 10% notified polymer) will be transferred to the packaging containers by a fully automated process by gravitational or mechanical means via a filtration system.

Samples will be taken from each batch for testing by laboratory technicians for quality control. Maintenance workers will clean the mixing equipment with water, and will collect the wastewater for subsequent disposal by licensed trade waste collectors.

End use

Professional applicators will apply the finished coating products (< 10% notified polymer) by brush or roller onto a variety of different substrates including wood, metal, stone and concrete. Applications will include coatings for doors, windows, indoor walls and floors and will be conducted within factories as well as in domestic situations.

6. HUMAN HEALTH IMPLICATIONS

6.1 Exposure assessment

6.1.1 Occupational exposure

NUMBER AND CATEGORY OF WORKERS

Category of Worker	Number	Exposure Duration (hours/day)	Exposure Frequency (days/year)
Transport	1-2	0	0
Paint formulation	1-2	2	60
Laboratory technicians	1-2	1	20
Paint packers	1-4	0.5	60
Paint sales	1-5	0.5	100
Professional painters	1-10	8	100

EXPOSURE DETAILS

Dermal and ocular exposure to the notified polymer (at \sim 55%) may occur when manually charging mixing vessels, and when disconnecting and connecting transfer lines.

Dermal and ocular exposure to the notified polymer (at < 10%) may occur when taking samples for testing, when cleaning the mixing equipment after use and when applying the coating products by brush or roller.

It is stated by the notifier that all workers are expected to wear personal protective equipment (coveralls, safety goggles and gloves) to limit exposure.

Workers will likely make dermal contact with the notified polymer after application. However, once the coatings have cured, the notified polymer will be reacted into the polymer matrix and will not be bioavailable.

6.1.2. Public exposure

DIY users will not use the coating products. The general public may make dermal contact with cured coating products on substrates, in which the notified polymer is reacted. In this form, the notified polymer will not be bioavailable.

6.2. Human health effects assessment

No toxicity data were submitted.

Irritation and Sensitisation

The MSDS provided for Polyamine 1420/46 states that the notified polymer is classified as corrosive (and therefore by nature a skin and eye irritant), and a sensitiser. This is consistent with the high content of secondary amines along the polymer backbone together with the high percentage of low molecular weight species (< 1000 Da); structural features that may predict corrosion and sensitisation.

Acute toxicity

The MSDS provided for Polyamine 1420/46 states that the notified polymer is classified as R21 (Harmful in contact with skin; $200 < \text{LD50} \le 2000 \text{ mg/kg}$) and R22 (Harmful if swallowed; $400 < \text{LD50} \ge 2000 \text{ mg/kg}$). These acute effects are likely to be due to the presence of a high concentration of low molecular weight species (< 1000 Da) in the notified polymer.

Health hazard classification

On the basis of the information given in the MSDS, the notified polymer is considered as hazardous under the *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004).

The classification and labelling details are:

- Xn; R21/22 Harmful in contact with skin and if swallowed
- Xi; R43 May cause sensitisation by skin contact
- C; R34 Causes burns
- Xi; R36 Irritating to eyes
- Xi; R38 Irritating to skin

6.3. Human health risk characterisation

6.3.1. Occupational health and safety

The notified polymer has been classified as a corrosive and a sensitiser, and the concentration during its lifecycle in Australia will be above the stated cut-off level for skin corrosion ($\geq 5\%$) and sensitisation ($\geq 1\%$). As a consequence, all workers where dermal and ocular exposure may occur are at potential risk from burns, irritation and sensitisation when handling the notified polymer as introduced and in finished coating products where the notified polymer is present at a concentration of > 1%.

Provided that all workers are expected to wear the proposed personal protective equipment to limit skin and eye contact and should follow the safe work practices as stated in the MSDS, the risk to workers, presented by the notified polymer is not considered to be unacceptable.

6.3.2. Public health

The risk to the health of the public by the notified polymer is not considered to be unacceptable under normal use conditions.

7. ENVIRONMENTAL IMPLICATIONS

7.1. Environmental Exposure & Fate Assessment

7.1.1 Environmental Exposure

RELEASE OF CHEMICAL AT SITE

Up to 5% of the notified polymer could be lost, possibly some to the sewer, during the cleaning of the mixing equipment. Residual material in the containers is expected to be about 2% of the import volume and is expected to be washed out with water and used in blending subsequent batches of the finished product, as could wastes from cleaning equipment.

RELEASE OF CHEMICAL FROM USE

It is estimated that up to 1% of the cross-linked notified polymer may be released to the sewer as a result of cleaning application equipment (brushes and rollers) with water.

RELEASE OF CHEMICAL FROM DISPOSAL

The majority of the waste notified polymer is expected to be sent to landfill as a dry solid, from flocculation of the wastewater and dried residues from the containers. The notified polymer as a dry solid is expected to remain associated with soils and sediments and would not be expected to leach into the aquatic environment. It is expected to degrade slowly by biotic and abiotic process to water vapour and oxides of carbon and nitrogen.

7.1.2 Environmental fate

When applied to substrates the notified polymer will cure, forming a solid inert film that is expected to share the fate of the substrate. This would not present a significant risk to the environment. Bioaccumulation of the notified polymer is unlikely due to high molecular weight of the notified polymer in its solid form.

7.1.3 Predicted Environmental Concentration (PEC)

Based on the use pattern and the waste generated it is estimated that up to 1% of the cross-linked notified polymer may end up in the sewer. The following PEC is calculated using the STP model:

Predicted Environmental Concentration (PEC) for the Aquatic Compartment		
Total Annual Import/Manufactured Volume	300,000	kg/year
Proportion expected to be released to sewer	1%	
Annual quantity of chemical released to sewer	3,000	kg/year
Days per year where release occurs	200	days/year
Daily chemical release:	15	kg/day
Water use	200	L/person/day
Population of Australia (Millions)	21.161	million
Removal within STP	0%	
Daily effluent production:	4,232	ML
Dilution Factor - River	1.0	
Dilution Factor - Ocean	10.0	
PEC - River:	3.5	μg/L
PEC - Ocean:	0.35	μg/L

7.2. Environmental effects assessment

The results from ecotoxicological investigations conducted on the monomers of the notified polymer are summarised in the table below as taken from the MSDS.

Endpoint	Result	Assessment Conclusion
Fish Toxicity	EC50 185 mg/L	The monomer* of the notified polymer is not
		harmful to fish.
Fish Toxicity	EC50 > 120 mg/L	The second monomer of the notified
		polymer is not toxic to fish.
Daphnia Toxicity	EC50 42 mg/L	The monomer* of the notified polymer is
		harmful to Daphnia.

^{* 5-}amino-1,3,3-trimethyl-cyclohexanemethanamine (IPDA)

The results indicate that the notified polymer is potentially harmful to *Daphnia*, as the cationic functionalities will be retained.

7.2.1 Predicted No-Effect Concentration

The toxicological data indicates that one of the monomers of the notified polymer is potentially harmful to *Daphnia*. However, a toxicity of 42 mg/L cannot be used to calculate a PNEC for the notified polymer as the data is for the toxicity of the monomer only.

7.3. Environmental risk assessment

When applied to substrates the notified polymer is expected to be cross-linked with the other ingredients of the epoxy coating formulation, forming a solid inert film that is expected to share the fate of the substrate.

The notified polymer is not expected to pose an unacceptable risk to the aquatic environment based on the proposed use pattern.

8. CONCLUSIONS AND REGULATORY OBLIGATIONS

Hazard classification

On the basis of the information given in the MSDS, the notified polymer is considered as hazardous under the *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004).

The classification and labelling details are:

- Xn; R21/22 Harmful in contact with skin and if swallowed
- Xi; R43 May cause sensitisation by skin contact
- C; R34 Causes burns
- Xi; R36 Irritating to eyes
- Xi; R38 Irritating to skin

and

As a comparison only, the classification of the notified polymer using the Globally Harmonised System for the Classification and Labelling of Chemicals (GHS) (United Nations, 2003) is presented below. This system is not mandated in Australia and carries no legal status but is presented for information purposes.

	Hazard category	Hazard statement
Health		
Sensitisation	1	May cause an allergic skin reaction
Corrosive	1	Causes severe skin burns and eye damage
Acute (dermal)	3	Toxic if swallowed
Acute (oral)	3	Toxic in contact with skin

Human health risk assessment

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

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

Environmental risk assessment

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

Recommendations

REGULATORY CONTROLS

Hazard Classification and Labelling

- Use the following risk phrases for products/mixtures containing the notified polymer:
 - R43 May cause sensitisation by skin contact
 - R34 Causes burns
 - R36 Irritating to eyes
 - R38 Irritating to skin
 - R22 Harmful if swallowed
 - R21 Harmful in contact with skin

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Xn; R21/22 C; R34 R43 R52-53

Conc ≥ 25%: C; R34; R21/22; R43

≥ 10%Conc < 25%: C; R34; R43

≥ 5%Conc < 10%: Xi; R36/38; R43

≥ 1%Conc < 5%: Xi; R43
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- The notified chemical should be classified as follows under the ADG Code:
 - Class 8 (Corrosive)

Health Surveillance

As the notified chemical is a skin 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
sensitisation.

CONTROL MEASURES

Occupational Health and Safety

- Employers should implement the following safe work practices to minimise occupational exposure during handling of the notified polymer as introduced and in the final coating products:
 - Where possible, automated processes should be used to reduce workers' exposure.
 - Avoid skin contact
 - Avoid eye contact
 - A shower station should be available

- Eye wash stations should be maintained
- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer as introduced and in the final coating products:
 - Coveralls
 - Safety goggles
 - Impermeable gloves

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 chemical 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 by landfill.

Storage

- The following precautions should be taken regarding storage of the notified chemical:
 - Do not store with acids.
 - Keep container tightly closed in a cool, well-ventilated area.

Emergency procedures

 Spills or accidental release of the notified polymer should be prevented from entering drains and waterways. Use absorbent material to collect and seal in properly labelled containers or drums for 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 Da.

or

- (2) Under Section 64(2) of the Act; if
 - the function or use of the chemical has changed from use as a hardener for epoxy-based coatings, or is likely to change significantly;
 - the amount of chemical being introduced has increased from 300 tonnes per annum, or is likely to increase, significantly;
 - if the chemical has begun to be manufactured in Australia;

- additional information has become available to the person as to an adverse effect of the chemical 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 polymer provided by the notifier was reviewed by NICNAS. The accuracy of the information on the MSDS remains the responsibility of the applicant.

BIBLIOGRAPHY

- FORS (Federal Office of Road Safety) (1998) Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG code), 6th Edition, Canberra, Australian Government Publishing Service
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