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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

FULL PUBLIC REPORT

Purmelt QR 3317 BR

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:

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Director
NICNAS

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1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)
Henkel Australia Pty Ltd (ABN 82 001 302 996)
135-141 Canterbury Road, KILSYTH, VIC 3137

NOTIFICATION CATEGORY
Limited: Synthetic polymer with Mn ≥ 1000 Da.

EXEMPT INFORMATION (SECTION 75 OF THE ACT)
Data items and details claimed exempt from publication: Chemical name, CAS number, Molecular formula, Structural formula, Molecular weight, Spectral data, Methods of detection and determination, Impurities/Residual monomers, Additives/Adjuvants, Polymer constituents, Introduction volumes and Use details.

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)
Variation to the schedule of data requirements is claimed as follows: Boiling Point, Vapour pressure, Water solubility, Hydrolysis as a function of pH, Partition Co-efficient, Adsorption/Desorption, Dissociation constant, Flammability limits, Autoignition temperature.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)
None

NOTIFICATION IN OTHER COUNTRIES
None

2. IDENTITY OF CHEMICAL

MARKETING NAME(S)
Purmelt QR 3317 BR

MOLECULAR WEIGHT
Mn > 1000 Da

ANALYTICAL DATA
Reference IR and GPC spectra were provided.

3. COMPOSITION

DEGREE OF PURITY > 90%

LOSS OF MONOMERS, OTHER REACTANTS, ADDITIVES, IMPURITIES
None under normal conditions of use.

DEGRADATION PRODUCTS
None under normal conditions of use. In the event of fire, combustion products of pyrolysis are likely to include oxides of carbon and nitrogen.

4. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AT 20°C AND 101.3 kPa: Off-white solid

Property	Value	Data Source/Justification
Melting Point	Approximately 60°C	MSDS
Boiling Point	Not determined	Notified polymer is a solid.
Density	1100 kg/m^3 at 20°C	MSDS
Vapour Pressure	< 10^{-8} kPa at 20°C	Estimated (EPA 2007)
Water Solubility	Not determined	Test not conducted due to the existence of reactive functionalities (with water). However, low water solubility is predicted based on the hydrophobic structure.
Hydrolysis as a Function of pH	Not determined	Test not conducted due to the predicted low water solubility. The notified polymer contains end functional groups that can readily react with water.
Partition Coefficient (n-octanol/water)	Not determined	A high partition coefficient is expected based on the low predicted water solubility.
Adsorption/Desorption	Not determined	The notified polymer is predicted to adsorb to soil from water due to the insolubility in water.
Dissociation Constant	Not determined	Dissociation is unlikely to occur under normal environmental pH range of 4–9 since no readily dissociable functionality exists.
Particle Size	Not determined	Notified polymer is a waxy solid.
Flash Point	> 200°C	MSDS
Flammability	Not determined	Not expected to be highly flammable based on flash point.
Autoignition Temperature	Not determined	Not expected to autoignite at ambient temperature and during normal use.
Explosive Properties	Not determined	Not expected to be explosive based on absence of explosive functional groups.

DISCUSSION OF PROPERTIES

The notified polymer is a solid at room temperature and has an extremely low vapour pressure, however heating the polymer may lead to the release of vapours containing monomeric isocyanates. The imported solution contains diphenylmethane-4,4'-diisocyanate (MDI).

Reactivity

Stable under normal environmental and usage conditions. The notified polymer is designed to react with atmospheric moisture as a part of the curing process.

5. INTRODUCTION AND USE INFORMATION

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

The notified polymer will be introduced as a > 90% component of finished and pre-packaged adhesive products.

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

Year	*1*	*2*	*3*	*4*	*5*
Tonnes	10-30	10-30	10-30	10-30	10-30

PORT OF ENTRY

Melbourne

TRANSPORTATION AND PACKAGING

Imported by ship in 17 kg blocks in metal drums and as large waxy pellets in 1 kg polyethylene packs. It will be transported from the dock to the notifier and to end-use sites by road or rail.

USE

The notified polymer is a > 90% component in ready-to-use polyurethane hotmelt adhesive for application in bookbinding.

OPERATION DESCRIPTION

There will be no reformulation or repackaging in Australia. At the end-use site, drums or packs will be moved from the storage area to the application unit and the seal of the drum/pack will be broken under a vented hood. For applications using drums, a plunger from the melter unit is inserted into the drum and the drum will be moved into an enclosed melter. Pellets will be manually emptied into the appropriate container and placed into the enclosed melter. The melter is set to the appropriate temperature to facilitate the delivery of the molten adhesive to the application head, which is then applied to the substrate as a molten bead of around 0.3-0.6 mm coat thickness. Between 50-80% of the bond strength is obtained in approximately 6 hours and complete curing occurs in 24 hours. Where UV lamps are used, crosslinking begins immediately and 80% of the curing process occurs within 3 minutes.

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 and Storage	10	1	200
Laminator Operators	2	6	100
Cleaning and Maintenance workers	1	0.5	100
Finished Good Quality Inspector	1	2	40

EXPOSURE DETAILS

Transport and storage workers are not likely to be exposed to the adhesive product containing the notified polymer except in the unlikely event of an accident.

The drum and packs containing the adhesive will be opened under a fume extraction system and the packs emptied into a suitable drum. A plunger is inserted into the drums and drums are immediately placed in the melter. At this stage the adhesive is a solid block or waxy solid pellets and volatile components are not expected to be released and available for inhalation exposure. Dermal exposure may occur during this stage and workers will wear nitrile gloves, safety glasses with side shield, and coveralls.

Melting of the adhesive is an enclosed process and confirmed via a computer monitor that relays information about molten adhesive egress through a bleeder valve at the top of the melter plunger. Once the melting has been confirmed, the bleeder valve is plugged and adhesive is automatically delivered to the application head.

The molten adhesive will be applied to the substrate under a ventilation hood to remove volatile components of the adhesive. Once binding is complete the adhesive is allowed to cure. The curing process takes 24 hours and during this time the books will be stored in ventilated areas of the warehouse.

At the end of the process, the adhesive feed to the application head is stopped and the remaining adhesive melt is allowed to run to the tray below the application head where it is allowed to cure overnight. The applicator roller is coated with cleaning agents and allowed to remain overnight. The cured adhesive is removed for disposal to landfill on the following day. Cleaning and maintenance workers are expected to wear organic vapour filter masks, goggles, gloves, protective overalls and safety footwear to avoid dermal, ocular and inhalation exposure.

6.1.2. Public exposure

Since the adhesive is not sold directly to the public, direct exposure to the notified polymer is not expected to occur, except in the unlikely event of a transport accident. Books and magazines containing the cured adhesive will be sold to the public but the polymer will be cured and crosslinked to form an inert matrix and will not be available for exposure.

6.2. Human health effects assessment

No toxicity data were submitted. In the absence of toxicological data on the notified polymer, the known general hazards of isocyanates have been considered, in particular, the hazards associated with MDI (a monomer of the notified polymer and present at a low concentration in the product).

The notified polymer is not expected to be absorbed across biological membranes to a significant extent, based on the high molecular weight (Mn > 1000 Da). However, due to the presence of low molecular weight species (5-10% with MW < 1000 Da), some absorption may occur.

Isocyanates are considered highly reactive and are known to be hazardous to human health. Generally, TDI (toluene diisocyanate) and HDI (hexamethylene diisocyanate) are viewed as posing a greater health hazard than other isocyanates such as MDI (NOHSC 1990), however the primary concern for all isocyanates is upper and lower respiratory tract toxicity, respiratory irritancy and respiratory sensitisation. Isocyanate exposure is the most common cause of occupational asthma around the world (Mapp et al 1988; Bernstein 1996) and no specific treatment is available for individuals who are sensitised. Individuals with a history of respiratory conditions such as asthma and hay fever may be more likely to develop isocyanate sensitivity (NOHSC 1990). Polymeric isocyanates are less volatile and contain less free isocyanate, and are therefore expected to be less of a vapour hazard. However, the UK Employment Medical Advisory Service believes polymeric isocyanate aerosols are capable of causing 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 be irritating to the skin and eyes and splashes in the eyes may lead to severe chemical conjunctivitis (NOHSC 1990). In addition isocyanates may cause 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, the presence of low molecular weight species means that these effects cannot be ruled out.

Health hazard classification

Based on the presence of the isocyanate functional group in the notified polymer, the notified polymer is classified as hazardous under the *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004).

Xn; R42 May cause sensitisation by inhalation

6.3. Human health risk characterisation

6.3.1. Occupational health and safety

Workers that are exposed to isocyanates may have a concentration-dependent risk of developing respiratory diseases such as bronchial asthma (Baur et al 1994) and often the only treatment for sensitised individuals is to completely remove the worker from the workplace to avoid exposure (Bernstein 1996). Therefore, measures should be in place to avoid workers from developing sensitisation. The engineering controls in place to reduce the exposure to vapours or aerosols of MDI, such as the enclosed melter, the local exhaust ventilation during the book-binding process, and the ventilation during curing, are expected to also minimise any potential inhalation exposure to the notified polymer. As the cleaning activities will be carried out after leaving the residual adhesive overnight the majority of the residual adhesive is expected to be cured. Cleaners are also expected to wear personal protective equipment (PPE) including an organic vapour filter mask. If it is determined that a significant amount of the isocyanate polymer and monomer remains uncured at this stage workers involved in cleaning equipment should wear respiratory apparatus that comply with the Australian Standard AS 1716 (NOHSC 1990). Therefore although the notified polymer is classified as a respiratory sensitiser, given the stated engineering controls and proposed use of PPE it is not likely to pose a significant respiratory sensitisation risk to workers.

The potential for the notified polymer to cause skin sensitisation, as well as skin and eye irritation could not be ruled out. Dermal and ocular exposure may occur during the opening of the packages containing the solid notified polymer, or during the cleaning of equipment. However, this exposure is expected to be minimised by the PPE to be worn, including nitrile gloves, coveralls and safety glasses.

Therefore when used under the conditions described the notified polymer is not expected to pose an unacceptable risk to workers.

6.3.2. Public health

The public will not be exposed to the notified polymer or isocyanate monomers; hence the risk to the public is very low.

7. ENVIRONMENTAL IMPLICATIONS

7.1. Environmental Exposure & Fate Assessment

7.1.1 Environmental Exposure

RELEASE OF CHEMICAL AT SITE

Release of the notified polymer from manufacturing or reformulating is not expected.

RELEASE OF CHEMICAL FROM USE

The application of the hot melt adhesive is very efficient with no waste being generated. Nearly all the polymer released to the environment will be the result of equipment cleaning and container residues. Waste generated from the equipment cleaning could be up to 1% of the total volume of notified polymer imported, which is allowed to cure and disposed of to landfill. The residue remaining in drums could be up to 1% and is allowed to moisture cure in the drum and disposed to landfill in the drum.

RELEASE OF CHEMICAL FROM DISPOSAL

The majority of the notified polymer will be applied to substrate as adhesive and will share the fate of the substrates. Most of the substrates will be sent to landfill, and some may also be recycled. During the paper recycling process, waste paper is repulped using chemical agents that enhance fibre separation, ink detachment and the whiteness of the paper. The aqueous wastes from this process are expected to be sent to the sewer. Negligible amounts of the notified polymer are expected to be released to the sewer since it is expected to be associated with the sludge that is generated during the washing process. This sludge will be dried and sent to landfill.

7.1.2 Environmental fate

No environmental fate data were submitted. In landfill, the notified polymer is not expected to leach and is likely to adhere to organic material, sediment and soil due to its expected low water solubility and high molecular weight. Over time, the polymer is expected to undergo biotic and abiotic degradation into small molecules of water and oxides of carbon and nitrogen. The potential for bioaccumulation of the polymer is low due to the high molecular weight.

7.1.3 Predicted Environmental Concentration (PEC)

The PEC has not been calculated since no significant release of the notified polymer to the aquatic compartment is expected to occur.

7.2. Environmental effects assessment

No ecotoxicity data were submitted. The polymer contains functionalities of high concern. However, this is not considered an issue given the reported use pattern of the polymer as hot melt adhesive in book binding and that very limited release to the aquatic environment is expected.

7.3. Environmental risk assessment

The risk of an adverse effect on the environment from the intended use of the notified polymer is acceptably low based on the reported use pattern.

8. CONCLUSIONS AND REGULATORY OBLIGATIONS

Hazard classification

Based on the available data the notified polymer is classified as hazardous under the *Approved Criteria for Classifying Hazardous Substances* [NOHSC:1008(2004)]. The classification and labelling details is:

Xn; R42 May cause sensitisation by inhalation

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 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:
  - Conc ≥ 1%: R42

- The following safety phrases should appear on the MSDS and label for the notified polymer:
  - S23 Do not breathe vapour or spray
  - S45 In case of accident or if you feel unwell seek medical advice immediately (and show the label where possible)

Health Surveillance

- As the notified polymer is a respiratory irritant and sensitiser, 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 isolation and engineering controls to minimise occupational exposure to the notified polymer:
  - Ventilation system including local exhaust ventilation.

- Employers should implement the following safe work practices to minimise occupational exposure during handling of the notified polymer:
  - Keep containers securely sealed and check regularly for spills and leaks.
  - Wash hands after handling the notified polymer, containers and equipment.

- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer:
  - Isocyanate-resistant gloves
  - Safety glasses with side shields
  - Overalls
  - Respiratory device (where there is a risk of inhalation exposure)

  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 volatile adhesive components during use of the notified polymer.

- 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 by landfill.

Storage

- The following precautions should be taken regarding storage of the notified polymer:
  - Check all containers against leakage and ensure lids and caps are tightly sealed
  - Store in a ventilated and bunded area.
  - Store in a cool dry place away from direct sunlight
  - Store away from acids, alkalis or amines.

Emergency procedures

- Spills or accidental release of the notified polymer should be handled by absorbing with solid decontaminant like soil or sand, 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;
  - the polymer is imported in a mixture that can be aerosolised;

or

(2) Under Section 64(2) of the Act; if
  - the function or use of the polymer has changed from hotmelt adhesive for book-binding, or is likely to change significantly;
  - the amount of polymer being introduced has increased from 30 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 the notified polymer and product containing the notified polymer provided by the notifier were reviewed by NICNAS. The accuracy of the information on the MSDS remains the responsibility of the applicant.

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