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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME (NICNAS)

FULL PUBLIC REPORT

Polymer T3918 in Pro-Seal Sealants

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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FULL PUBLIC REPORT

Polymer T3918 in Pro-Seal Sealants

1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT
PPG Industries Australia Pty Ltd (ABN 82 055 500 939)
21-23 Ovata Drive
Tullamarine VIC 3043

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, Other Names, CAS Number, Structural Formula, Molecular Weight, Spectral Data, Purity, Residual Monomers, Additives and Adjuvants, Import Volume, and Identity of Manufacturers/Recipients

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)

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

Vapour pressure, Hydrolysis as a function of pH, Adsorption/desorption, Dissociation constant, Flammability, Autoignition temperature.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT None

NOTIFICATION IN OTHER COUNTRIES Canada (1999)

2. IDENTITY OF CHEMICAL

Marketing Name T3918 T3921

 $\begin{array}{l} Molecular \ Weight \\ Mn > 1,000 \ Da \end{array}$

ANALYTICAL DATA

Reference HPLC and GPC spectra were provided.

3. COMPOSITION

DEGREE OF PURITY > 95%

HAZARDOUS IMPURITIES/RESIDUAL MONOMERS None

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

4. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AT 20°C AND 101.3 kPa Brown viscous liquid

Property	Value	Data Source/Justification
Melting Point/Freezing Point	Not determined	Test not conducted.
Pour Point	-2.8°C	Measured
Softening Point	-15.3°C	Measured
Glass Transition Temperature	-40.6°C	Measured
Boiling Point	182°C	MSDS
Density	1300 kg/m^3	Measured
Viscosity	120 Pa.s at 25°C	Measured
Vapour Pressure	< 1.3x10 ⁻⁹ kPa	Estimated. Molecular weight is > 1000 Da, which indicates that it is likely to have a vapour pressure of $< 1.3 \times 10^{-9}$ kPa (USEPA, 2007).
Water Solubility	252 mg/L	Measured
Hydrolysis as a Function of pH	Not determined	No hydrolysable functionalities
Partition Coefficient (n-octanol/water)	log Pow < 1.76 for 80% of notified polymer	Measured
Adsorption/Desorption	$\log K_{\rm oc} < 3$	Estimated based on predicted low log Pow
Dissociation Constant	Not determined	(despite its low water solubility). Dissociation may occur, particularly on hydrolysis, however, it is likely to be limited due to low water solubility. Not likely to dissociate in the pH range of 4-9.
Particle Size	Not determined	N/A. The notified polymer is a liquid at
1 42 444 5 5 5 5	1,00 000111111100	room temperature.
Flash Point	132.2°C	Measured
Flammability	Not determined	Based on the flash point the notified
y		polymer is not classified as flammable.
Autoignition Temperature	Not determined	The autoignition temperature will be > 132°C, based on its flash point.
Explosive Properties	Not expected to be explosive	Contains no explosophores, and is imported as a paste without dust explosive hazard.
Refractive Index	1.5901	Measured
Ash Content	None	Measured
Mercaptan Equivalent α	3808	Measured

 $^{^{\}alpha}$ The measured Mercaptan Equivalent indicates that there is a significant quantity of free thiol groups within the notified polymer.

DISCUSSION OF PROPERTIES

For full details of tests on physical and chemical properties, please refer to Appendix A.

Based on the flash point, the notified polymer is not classified as flammable according to the Australian Dangerous Goods classification (FORS, 2007). However, it is classified as a C1 combustible liquid according to the *National Standard for the Storage and Handling of Workplace Dangerous Goods* (NOHSC 2001).

Loss of Monomers, Other Reactants, Additives, Impurities

Stable under normal conditions of use. Following curing of the notified polymer, losses due to volatility, exudation or leaching are not expected to occur.

Degradation Products

None expected under normal conditions of use. In the event of a fire, combustion products of pyrolysis (oxygen limited) are likely to include miscellaneous hydrocarbons, water and oxides of carbon and sulfur.

Reactivity

The notified polymer is stable under normal conditions and reactivity to water and air is negligible.

5. INTRODUCTION AND USE INFORMATION

Mode of Introduction of Notified Chemical (100%) Over Next 5 Years

The notified polymer will be imported in a range of sealant products at concentrations between 1 and 90%. One

such product, Pro-Seal 870, is a two-part sealant product, with Part B typically containing the notified polymer at concentrations of 1-10%, and Part A not containing the notified polymer.

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

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

PORT OF ENTRY

All major seaports throughout Australia, especially Melbourne.

IDENTITY OF MANUFACTURER/RECIPIENTS

PPG Industries Australia Pty Ltd.

TRANSPORTATION AND PACKAGING

The products containing the notified polymer will be imported into Australia in 20 L containers, 200 L drums, or plastic applicator containers. The product will then be transported by road or rail to customers. The applicator products will be sold in the original package.

USE

The notified polymer is used in sealant products for aerospace industry applications.

OPERATION DESCRIPTION

No manufacture or reformulation of the notified polymer will occur in Australia.

Repackaging

Lids will be removed from the import containers, and transfer to a hopper will be performed using either a drum pump or a drum lift (for the 20L containers). The sealant product containing the notified polymer will then be extruded into two-compartment plastic applicator tubes. The tube compartment containing the notified polymer (Part B of the sealant product) will then be manually joined to the compartment containing Part A and placed within a Mylar foil bag (heat-sealed, nitrogen-filled and airtight). The tubes will then be packaged into cardboard boxes and may be stored on-site prior to distribution to customers. Small samples are used for quality control testing for shelf life.

Application

At the customer sites, prior to application of the sealant, Part B of the two-part sealant product will be injected into, and mixed manually with, Part A within the plastic applicator. Alternatively, mixing may be performed automatically by connecting the spoke of the applicator to an automatic mixer. A nozzle will then be attached to the applicator and a pressure gun will be used to pump the sealant out. Following application the equipment may be cleaned to remove any excess sealant.

The sealant will then be applied directly to the aerospace components, and may include application in confined spaces, such as fuel tanks.

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 Personnel	30	5	150
Manufacturing Personnel – Repackaging	25	8	250
Quality Assurance Personnel	10	2	100
Manufacturing Personnel – Application	50	6	200

EXPOSURE DETAILS

Transport and Storage

The notified polymer will be sealed within storage containers and as such, transport and storage workers are not expected to be exposed to the notified polymer, except if the packaging were accidentally breached.

Repackaging

During repackaging of the sealant products into applicator tubes accidental dermal or ocular exposure to the notified polymer (typically at concentrations of <10%, though possibly up to 90%) may occur. Significant exposure would be limited by performing such operations under general exhaust ventilation and the use of appropriate personal protective equipment (PPE) such as safety glasses, safety shoes, coveralls, apron and chemical resistant gloves.

Exposure of quality control personnel during testing may occur but is expected to be low as PPE will be worn, including chemical resistant gloves, safety shoes, eye protection and laboratory coats.

Application

Exposure to the notified polymer (typically at concentrations of <10%, though possibly up to 90%) during mixing of Part A and Part B of the sealant product is expected to be minimal, as it occurs within an enclosed applicator tube. The applicator tube allows the sealant product to be directly applied through a nozzle to the aerospace component, reducing worker exposure. Exposure will be further minimised by performing the operations under general exhaust ventilation. The use of PPE will be dependent upon the other components of the sealant products and the type of aerospace part to which it is applied, eg. in confined spaces, ventilation masks are likely to be worn.

6.1.2. Public exposure

The notified polymer will not be supplied directly to the public, so there will be no public exposure except in the occurrence of an accidental spill during transport. The public may come into contact with the notified polymer where it is used on aircrafts. However, in this form the notified polymer will be cured within the sealant, and will not be available for exposure.

6.2. Human health effects assessment

No toxicity data were submitted.

The notified polymer contains disulfide and thiol functional groups. Groups of this type are structural alerts for irritation or corrosion (Hulzebos 2005), and sensitisation (Barratt 1994). Whilst the relatively high molecular weight of the notified polymer may reduce the possibility of such effects, it should be noted that the proportion of low molecular weight species is significant (15-20% <1000, 10-15% <500). In addition, the chemical properties of the notified polymer, such as its water solubility and estimated partition coefficient (log Pow = 1 - 4 for majority of the notified polymer mixture) suggest that some dermal absorption may be possible. Hence, irritation, corrosion, and sensitisation effects of the notified polymer cannot be ruled out. It is noted that there have been several reports of skin effects such as contact allergies caused by polysulfide polymers, particularly from sealants used in the aircraft industry (Wilkinson 1993, Bruze 1996).

Classification

Based on the anticipated irritation (skin and eyes) and skin sensitisation effects, the notified polymer should be classified as hazardous under the *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004). The notifier has independently applied hazard classifications to the notified polymer. The following risk phrases should be applied to the notified polymer:

R43 May cause sensitisation by skin contact R36/38 Irritating to eyes and skin

6.3. Human health risk characterisation

6.3.1. Occupational health and safety

Dermal and ocular exposure of workers to the notified polymer may occur during its handling (repackaging and application). Given the relatively high concentrations at which the notified polymer may be present during such handling operations (up to 90% in some cases), skin and eye irritation, and/or skin sensitisation cannot be ruled out. Exposure is expected to be reduced by the use of engineering controls, the wearing of appropriate PPE and the enclosed nature of the applicator tubes. Whilst such measures should act to mitigate the health concerns, care should be taken by workers when handling products containing the notified polymer. Overall, the risk to occupational health and safety from the notified polymer is not considered to be unacceptable.

6.3.2. Public health

Members of the public will only occasionally come into contact with aerospace parts on which the notified polymer has been cured. As such, the risk to public health is considered to be low.

7. ENVIRONMENTAL IMPLICATIONS

7.1. Environmental Exposure & Fate Assessment

7.1.1 Environmental Exposure

RELEASE OF CHEMICAL AT SITE

The notified polymer will be imported in 20 L containers or 200 L drums and will not be manufactured in Australia. Local operations will include transport, storage and repackaging. Release to the environment during shipping, transport and warehousing will only occur in the unlikely event of accidental spills or leaks of the packaging.

The notified polymer is of high viscosity and release via evaporation is unlikely to occur. During repackaging approximately 1% (10 kg per annum) of the notified polymer will be spilt. These spills will be contained within plant bunding and disposed of by a licensed waste contractor. Less than 1% will be wasted through equipment cleaning. These washes will be stored in containers and disposed of by licensed waste contractors. Approximately 1% of the notified polymer may remain as residue in the drums. These will undergo drum recycling or be removed by licensed waste contractors. There will be no release to the environment or waterways during this process.

RELEASE OF CHEMICAL FROM USE

During use there will be minimal release of the notified polymer. However, as a worst case scenario, release of 1% of the notified polymer could be assumed during spills. This will be contained and disposed of by a licensed waste contractor. Approximately 1% (10 kg per annum) may remain in the tubing; this will be disposed of to licensed waste contractors. An additional 1% of the notified polymer may be lost during cleaning. This may be released in waterways. However, the release will be diffuse throughout Australia and is not likely to impact the environment.

RELEASE OF CHEMICAL FROM DISPOSAL

The notified polymer released on repackaging or during application will be disposed of predominantly by licensed waste contractors to landfill. There may be some drum recycling and minimal exposure to the environment that may occur as the result of cleaning of equipment in small applicator areas. Empty applicators will be land filled.

7.1.2 Environmental fate

The eventual fate of the notified polymer will ultimately depend on the substrate to which it is applied. At the end of the substrate's useful life, it is likely to undergo recycling processes and the notified polymer will be thermally decomposed to various oxides of carbon, sulfur, and water.

7.1.3 Predicted Environmental Concentration (PEC)

No significant concentrations of the notified polymer are expected in the aquatic environment based on the limited possibility for release and the low water solubility of the notified polymer. Therefore, the PEC for the notified polymer has not been calculated.

7.2. Environmental effects assessment

No ecotoxicity data were submitted. Non-ionic polymers of MW > 1000 are of limited concern to the aquatic compartment.

7.3. Environmental risk assessment

The notified polymer is not considered to pose an unacceptable risk to the environment based on its reported use pattern and its predicted low toxicity.

8. CONCLUSIONS AND REGULATORY OBLIGATIONS

Hazard classification

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

R43 May cause sensitisation by skin contact R36/38 Irritating to eyes and 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

The notified polymer is not considered to pose a risk to the environment based on its reported use pattern.

Recommendations

REGULATORY CONTROLS
Hazard Classification and Labelling

- Use the following risk phrases for products/mixtures containing the notified polymer:
 - Concentration ≥ 1% R43 May cause sensitisation by skin contact
 - Concentration ≥ 20% R36/38 Irritating to eyes and skin
- The following safety phrases should appear on the MSDS and label for the product containing the notified polymer:
 - S24 Avoid contact with skin
 - S36 Wear suitable protective clothing
 - S37 Wear suitable gloves

Health Surveillance

 As the notified polymer is a potential 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 skin 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:
 - Minimise spills and drips
 - Avoid skin and eye contact
- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer:
 - Safety glasses

- Gloves
- Coveralls

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 to landfill.

Emergency procedures

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

Regulatory Obligations

Secondary Notification

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

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

- (1) Under Section 64(1) of the Act; if
 - the polymer has a number-average molecular weight of less than 1000;

or

- (2) Under Section 64(2) of the Act; if
 - the function or use of the chemical has changed from a sealant product for aerospace industry applications, or is likely to change significantly;
 - the amount of chemical being introduced has increased from one tonne 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.

No additional secondary notification conditions are stipulated.

Material Safety Data Sheet

The MSDS of the notified polymer and products 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.

APPENDIX A: PHYSICAL AND CHEMICAL PROPERTIES

Pour Point -2.8°C

Method Thermomechanical Analysis

A test report was not provided with the notification submission. The value, test method Remarks

and test result were provided as attachments to the Canada substance notification.

Products Research and Chemical Corporation (1988) **Test Facility**

Softening Point -15.3°C

Method Thermomechanical Analysis

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

-40.6°C **Glass Transition Temperature**

Method Differential Scanning Calorimetry

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Products Research and Chemical Corporation (1988) **Test Facility**

Density 1300 kg/m^3

Method ASTM E-12

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

Viscosity 120 Pa.s at 25°C

Method ASTM 1824

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

Water Solubility 252 mg/L

Method OECD TG 120 Solution/Extraction Behaviour of Polymer in Water based on OECD TG

105 Water Solubility.

Remarks Flask Method. As the test material was a liquid, Method TG 120 was not applicable, and

> solution/extraction behaviour was investigated by alternative methods. The concentration of the notified polymer in water was determined by gravimetric analysis. It was not

possible to obtain a true solution of notified chemical in water with use of a co-solvent.

SafePharm (2007) **Test Facility**

Hydrolysis as a Function of pH Measurement could not be conducted

Remarks It was difficult to obtain accurate measurements by GPC, given that if the notified

> polymer was to hydrolyse, the degradation products could elute at similar times to the parent material. The limited solubility of the notified polymer in water also caused in

difficulties in performing the test.

SafePharm (2007) **Test Facility**

Partition Coefficient (nlog Pow < 1.76 for 80% of the notified polymer, with 20% > 6.5octanol/water)

OECD TG 117 Partition Coefficient (n-octanol/water). Method

Remarks HPLC Method. Test conducted at 40°C using tetrahydrofuran/osmosis water=50/50 (v/v) as the mobile phase. Thiourea was used for determination of the dead time.

Tetrahydrofuran was used as solvent of the notified polymer.

Test Facility SafePharm (2007)

Flash Point 132.2°C

Method Pensky-Martin Closed Cup ASTM D-93

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

Refractive Index 1.5901

Method ASTM 1747 (25°C)

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

Ash Content None

Method ASTM D-1131

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

Acid Number 8.7 mg KOH/g

Method ASTM D-1638

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

Mercaptan Equivalent 3808

Method Iodine Titration

Remarks A test report was not provided with the notification submission. The value, test method

and test result were provided as attachments to the Canada substance notification.

Test Facility Products Research and Chemical Corporation (1988)

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