

File No LTD/1135

September 2004

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME
(NICNAS)**

FULL PUBLIC REPORT

Polymer in Pliogrip Adhesives

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 and Heritage.

For the purposes of subsection 78(1) of the Act, this Full Public Report may be inspected at:

Library
National Occupational Health and Safety Commission
25 Constitution Avenue
CANBERRA ACT 2600
AUSTRALIA

To arrange an appointment contact the Librarian on TEL + 61 2 6279 1161 or + 61 2 6279 1163.

This Full Public Report is 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
Chemicals Notification and Assessment**

TABLE OF CONTENTS

FULL PUBLIC REPORT	4
1. APPLICANT AND NOTIFICATION DETAILS	4
2. IDENTITY OF CHEMICAL	4
3. COMPOSITION	5
4. INTRODUCTION AND USE INFORMATION	5
5. PROCESS AND RELEASE INFORMATION	5
6. PHYSICAL AND CHEMICAL PROPERTIES	7
7. TOXICOLOGICAL INVESTIGATIONS	9
8. ENVIRONMENT	10
9. RISK ASSESSMENT	11
10. CONCLUSIONS – ASSESSMENT LEVEL OF CONCERN FOR THE ENVIRONMENT AND HUMANS	12
11. MATERIAL SAFETY DATA SHEET	12
12. RECOMMENDATIONS	13
13. BIBLIOGRAPHY	14

FULL PUBLIC REPORT

Polymer in Pliogrip Adhesives

1. APPLICANT AND NOTIFICATION DETAILS

APPLICANT(S)

Ashland Pacific Pty Ltd (ACN 000 075 641), Sir Thomas Mitchell Road, Chester Hill NSW 2162.

NOTIFICATION CATEGORY

Limited: Polymer with NAMW ≥ 1000 (greater than 1 tonne per year).

EXEMPT INFORMATION (SECTION 75 OF THE ACT)

Data items and details claimed exempt from publication: Chemical name, molecular and structural formulae, molecular weight, spectral data, polymer constituents, impurities and percentage of the polymer in products.

VARIATION OF DATA REQUIREMENTS (SECTION 24 OF THE ACT)

No variation to the schedule of data requirements is claimed.

PREVIOUS NOTIFICATION IN AUSTRALIA BY APPLICANT(S)

Commercial Evaluation Category Permit (Permit No. 507).

NOTIFICATION IN OTHER COUNTRIES

None.

2. IDENTITY OF CHEMICAL

OTHER NAME(S)

Isocyanate/polyol resin.

MARKETING NAME(S)

The notified polymer will be present in Pliogrip 7400, 7600 and 7700 series products.

Pliogrip 7400 (Part A – isocyanate rich component).

Pliogrip 7651, 7652, 7655, 7654 or 7659 (Part B – polyol curatives)

Pliogrip 7651, 7652, 7655, 7654 and 7659 belong to the 7771, 7773, 7779, 7770 and 7779L series products, respectively.

MOLECULAR WEIGHT

Number Average Molecular Weight (Mn)	> 1000
Weight Average Molecular Weight (Mw)	> 1000
% of Low MW Species < 1000	< 10
% of Low MW Species < 500	0

METHODS OF DETECTION AND DETERMINATION

ANALYTICAL METHOD	IR spectroscopy.
Remarks	A reference spectrum was provided.

3. COMPOSITION

DEGREE OF PURITY

> 50%

HAZARDOUS IMPURITIES/RESIDUAL MONOMERS

The isocyanate rich component of the notified polymer contains up to 50% of isocyanate monomer – polymeric MDI (CAS No. 9016-87-9) – see MSDS for Pliogrip 7400.

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

None.

ADDITIVES/ADJUVANTS

None.

DEGRADATION PRODUCTS

None known.

LOSS OF MONOMERS, OTHER REACTANTS, ADDITIVES, IMPURITIES

The residual monomers may be lost to the environment when the polymer or products containing it are in the liquid state. However, once the two parts of the adhesive are mixed and cured, the monomers will be trapped in the solid matrix.

4. INTRODUCTION AND USE INFORMATION

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

The notified polymer will be imported as a component of a 2 part adhesive system in a purpose built cartridge system consisting of two separate chambers, one chamber containing the isocyanate-rich prepolymer and the other chamber the curative polyol-rich prepolymer. The total volume of the cartridge system will be 660 mL.

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

<i>Year</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
<i>Tonnes</i>	< 10	< 10	< 10	< 10	< 10

USE

Component of structural adhesive.

5. PROCESS AND RELEASE INFORMATION

5.1. Distribution, transport and storage

PORT OF ENTRY

Sydney.

IDENTITY OF MANUFACTURER/RECIPIENTS

Ashland Pacific Pty Ltd, Sir Thomas Mitchell Road, Chester Hill NSW 2162.

TRANSPORTATION AND PACKAGING

The notified chemical will be imported in a finished product as purpose-built cartridges which will be packed in sturdy cardboard boxes and will be transported by ship and internally by road.

5.2. Operation description

No reformulation or repackaging of the product occurs in Australia. The product is delivered to the end-user as imported into Australia. Local operations will involve use of the adhesive system in vehicle manufacturing and repair.

5.3. Occupational exposure

Number and Category of Workers

<i>Category of Worker</i>	<i>Number</i>	<i>Exposure Duration</i>	<i>Exposure Frequency</i>
Transport and warehouse	10-15	2 - 8 hours/day	36 days/year
Manufacturing workers	Approx 1000	10 - 30 minutes	220 days/year

Exposure Details

Transport and storage workers will be handling the sealed cartridges containing the notified polymer at a concentration of up to 7%. Exposure to the notified polymer may occur during an accident where the cartridges are damaged. Route of exposure is likely to be dermal. These workers will wear work clothing/overalls and safety boots.

Vehicle manufacturing workers place the cartridge system into the applicator gun, remove the end seal and extrude a small quantity of adhesive by squeezing the applicator gun trigger until a uniform mixing (1:1 ratio) of the two parts (as judged by the colour) is achieved. The nozzle is then attached to the cartridge. The adhesive is viscous and it is extruded in a continuous stream onto the surface of the substrate in a controlled manner. The working time is 3 minutes, clamp time is 10 minutes and the adhesive is fully cured in 30 minutes. Thus exposure time per application is minimal. Excess material is removed by wiping with a cloth. The main route of exposure to the notified polymer will be dermal. Workers will wear protective clothing and footwear as well as safety glasses and gloves. If local and general ventilation is insufficient to control exposure to isocyanate monomer, a suitable respirator will be used.

5.4. Release

RELEASE OF CHEMICAL AT SITE

The notified chemical is not intended to be manufactured or reformulated in Australia.

RELEASE OF CHEMICAL FROM USE

Release of the notified polymer will occur as a result of damaged cartridges, use of excess adhesive, residues in the empty cartridges and final disposal of treated vehicles. It is estimated that approximately 0.5% of the import volume (50 kg/year) may be released from accidental spills and leaks. As the adhesive is viscous, any spilt or leaking material can be easily contained and collected by using a small cloth for small leaks and sand for larger leaks. During use, excess adhesive will be wiped off with a cloth. As the two parts of the adhesive have been mixed, the adhesive will cure to form a solid matrix. The cloth will be disposed of to landfill. Release from excess adhesive is expected to account for 5% of import volume (500 kg/year). The residues in the empty cartridges are expected to be 3% of import volume (300 kg/year). The empty cartridges will be disposed of to landfill. The notified polymer used on the vehicles will have the same fate as the vehicles or the treated part of the vehicles. This would result in either landfill, or destruction on recycling of the vehicle parts. There will be no release of the notified polymer to the sewer or receiving water.

5.5. Disposal

The notified polymer will be disposed of by landfill or incineration.

5.6. Public exposure

The notified chemical will not be manufactured, reformulated or packaged in Australia. The public may be exposed to the notified polymer in the unlikely event of an accident during transport involving extensive breakage of cartridges.

The adhesive products containing the notified polymer are for professional use and will not be sold to the public. Furthermore, the adhesive is used in manufacture of heavy vehicles and is applied to concealed areas. Once cured, the polymer will be in an inert solid matrix. Thus, public exposure will not be significant.

6. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa	Viscous liquid.
Boiling Point	> 200°C at 101.3 kPa
Remarks	Pliogrip 7400.
Density	1288 kg/m ³ at 25°C.
Remarks	Pliogrip 7400.
Vapour Pressure	Not determined.
Remarks	Expected to be low due to high molecular weight.
Water Solubility	Not determined.
Remarks	<p>Isocyanate-rich component: The notified polymer is synthesised in the presence of large excess MDI and is not isolated. The isocyanate groups in MDI and the prepolymer will react with water. The polymer is likely to undergo cross-linking and form a solid mass. Thus, a reliable measurement for water solubility cannot be obtained.</p> <p>Polyol-rich component: The notified polymer is synthesised in the presence of a large excess of polyol and is not isolated. Any measurement of water solubility will be obscured by that of the polyol and a reliable value for the water solubility of the notified polymer cannot be obtained.</p>
Hydrolysis as a Function of pH	Not determined
Remarks	Due to the expected low water solubility of the notified chemical, it is not expected to hydrolyse under environmental conditions (pH 4-9) in spite of the presence of a potentially hydrolysable group.
Partition Coefficient (n-octanol/water)	Not determined
Remarks	As indicated in water solubility section, the solubility of the notified polymer could not be determined. However, based on the chemical structure provided, it is likely that the notified chemical would partition to the organic phase due to its mainly hydrophobic nature.
Adsorption/Desorption	Not determined
Remarks	While this was not attempted, it is expected that the polymer will adsorb to or associate with soils and sediments due to its mainly hydrophobic structure.
Dissociation Constant	Not determined
Remarks	No portion of the molecule is expected to be ionised in the environmental pH range of 4-9.
Particle Size	Not determined.
Remarks	Notified chemical is in liquid form.
Flash Point	> 93°C at 101 kPa.
METHOD Remarks	EC Directive 92/69/EEC A.9 Flash Point. Setaflash closed cup.

Flammability Limits	Not determined.
----------------------------	-----------------

Remarks	Not expected to be flammable.
---------	-------------------------------

Autoignition Temperature	Not determined.
---------------------------------	-----------------

Explosive Properties	Not determined.
-----------------------------	-----------------

Remarks	Not expected to be explosive.
---------	-------------------------------

Reactivity

Remarks	The notified polymer (in isocyanate-rich form) is expected to react with water and undergo cross-linking. The polymer will also react with strong oxidising materials, alcohols, amines, alkalis or acids.
---------	--

7. TOXICOLOGICAL INVESTIGATIONS

No toxicity data were submitted.

8. ENVIRONMENT

8.1. Environmental fate

No environmental fate data were submitted

8.2. Ecotoxicological investigations

No ecotoxicity data were submitted

9. RISK ASSESSMENT

9.1. Environment

9.1.1. Environment – exposure assessment

The notified polymer will be imported as a finished product in purpose-built and sealed cartridges. There will be no formulation or repacking in Australia. Release of the notified polymer will occur as a result of damaged cartridges (50 kg/year), use of excess adhesive (500 kg/year), residues in the empty cartridges (300 kg/year) and final disposal of treated vehicles to landfill or for recycling. Any leaks or spills will be easily contained and collected and disposed of to landfill. The adhesive will be cured to form a solid which ultimately will be disposed of to landfill. The empty cartridges will be disposed of to landfill. All the polymer used on the vehicles will have a similar fate as the vehicles or treated part of the vehicle and will be in the cured form when it is released. There will be no release of the notified polymer to sewer or to receiving waters.

9.1.2. Environment – effects assessment

No data were provided for the notified polymer. Given the reported use pattern, the notified polymer is not expected to enter the aquatic environment and pose a hazard to aquatic organisms.

9.1.3. Environment – risk characterisation

Based on the reported use pattern, most of the notified polymer will be in a cured form when disposed of to landfill. There will be no release of the notified polymer in the aquatic environment. Therefore, there is a low risk to the environment from the use proposed.

9.2. Human health

9.2.1. Occupational health and safety – exposure assessment

Exposure to the notified polymer is expected mainly to be dermal and can occur when the adhesive containing it is extruded from the imported cartridge on to the vehicle to which it is applied. As the working time is 3 minutes, exposure will mainly occur when wiping off excess adhesive. The notifier claims that gloves will be worn by workers to prevent dermal exposure. Adhesive on rags used to wipe off excess should cure in 3 minutes. Residues in cartridges should not be available for exposure.

Inhalation exposure to the notified polymer is unlikely.

9.2.2. Public health – exposure assessment

Exposure to the public is only likely in the event of a transport accident. Otherwise, the adhesive will not be sold to the public. The cured adhesive on the heavy vehicles to which it is applied is in concealed areas and in any case is not bioavailable.

9.2.3. Human health - effects assessment

The notified polymer itself in the polyol-rich form would not be predicted to be hazardous. However, the excess isocyanate in the isocyanate-rich polymer is listed on the NOHSC List of Designated Hazardous Substances (NOHSC, 2004) under diphenylmethane diisocyanate (isomers and homologues), CAS No. 9016-87-9. As the amount of excess isocyanate is greater than 25% the following risk phrases would be assigned: R20 - Harmful by inhalation, R36/37/38 - Irritating to eyes, respiratory system and skin and R42/43 - May cause sensitisation by inhalation and skin contact. The isocyanate end groups in the isocyanate-rich polymer are expected to have similar properties, but the low volatility make inhalation exposure unlikely.

Based on the available data, the notified polymer in the polyol-rich form is **not classified** as a hazardous substance in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2002). The notified polymer in the isocyanate-rich form may be treated as a mixture of the polyol and excess isocyanate monomer.

9.2.4. Occupational health and safety – risk characterisation

Occupational asthma has been observed in workplaces with atmospheric concentrations of toluene diisocyanate ranging from 1 to 25 ppb (median 5 ppb) (Bakke, J V, 2001). It is reasonable to suppose that a similar range of atmospheric concentrations of MDI would produce the same outcome. Although the atmospheric concentrations of MDI resulting from use of the notified polymer are unknown, they could be expected to be at the lower end of the range based on its lower volatility and the fact that curing of the adhesive is designed to be rapid. In the absence of quantitative monitoring data it must be assumed there is a risk of occupational asthma from use of the notified chemical on a long term basis. This is so despite the fact that the risk of occupational asthma from isocyanate exposure is greater if the exposure is short term and high level as opposed to long term and low level (Bakke, J V, 2001).

Before the adhesive is properly mixed as judged by colour, a small amount may be extruded as waste. In this case there is potential for exposure to uncured MDI unless the residue is properly disposed of.

As excess adhesive is wiped off using a rag, there is potential for dermal exposure and a risk of skin irritation and sensitisation.

9.2.5. Public health – risk characterisation

Public exposure to the notified chemical is only possible in the event of a transport accident and rupture of import containers. Once the adhesive containing the notified chemical is applied to vehicles and cured, public exposure is unlikely and in any case the notified chemical is not bioavailable.

10. CONCLUSIONS – ASSESSMENT LEVEL OF CONCERN FOR THE ENVIRONMENT AND HUMANS

10.1. Hazard classification

Based on the available data the notified polymer in the polyol-rich form is not classified as hazardous under the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2002). However, the isocyanate-rich component of the adhesive is classified as hazardous. The classification and labelling details are:

R20 - Harmful by inhalation,
R36/37/38 - Irritating to eyes, respiratory system and skin and
R42/43 - May cause sensitisation by inhalation and skin contact.

10.2. Environmental risk assessment

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

10.3. Human health risk assessment

10.3.1. Occupational health and safety

There is Moderate Concern to occupational health and safety under the conditions of the occupational settings described.

10.3.2. Public health

There is Negligible Concern to public health when used as indicated.

11. MATERIAL SAFETY DATA SHEET

11.1. Material Safety Data Sheet

The MSDS of the [products containing the notified polymer](#) provided by the notifier [were](#) in accordance with the NOHSC *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 2003). [They are](#) published here as a matter of public record. The accuracy of the information on the MSDS remains the responsibility of the applicant.

11.2. Label

The label for a [product containing the notified polymer](#) provided by the notifier was in accordance with the NOHSC *National Code of Practice for the Labelling of Workplace Substances* (NOHSC, 1994). The accuracy of the information on the label remains the responsibility of the applicant.

12. RECOMMENDATIONS

The following recommendations relate to the isocyanate-rich notified polymer containing approximately 50% excess isocyanate. Although the adhesive contains the notified polymer at a low level (7%), in the absence of certain knowledge of likely atmospheric concentrations of isocyanate in the workplace and in view of the serious consequences of isocyanate-induced respiratory sensitisation, a conservative approach to risk management should be taken.

CONTROL MEASURES

Occupational Health and Safety

- Employers should implement the following engineering controls to minimise occupational exposure to the notified polymer in Pliogrip adhesives:
 - Good general ventilation and local exhaust ventilation where practicable.
- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified polymer in Pliogrip adhesives:
 - Supplied air respiratory protection and protective clothing, gloves and footwear impervious to isocyanate-containing compounds. The open points at the interface between different forms of protective clothing should be sealed.

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

- Atmospheric or biological monitoring should be conducted by qualified professionals to gauge potential workplace atmospheric concentrations of isocyanate during use of the notified polymer.
- 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 NOHSC *Approved Criteria for Classifying Hazardous Substances*, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.
- Preplacement and periodic medical surveillance programs should be conducted for all workers potentially exposed to isocyanates. Emphasis should be placed on pre-existing respiratory and/or allergic conditions and lung function tests.

Environment

Disposal

- The notified chemical should be disposed of by landfill or incineration

Emergency procedures

- Absorb with an inert material and put the spilled material in an appropriate waste disposal. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sewer system.

12.1. Secondary notification

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

(1) Under Section 64(2) of the Act:

- if any of the circumstances listed in the subsection arise.

The Director will then decide whether secondary notification is required.

No additional secondary notification conditions are stipulated.

13. BIBLIOGRAPHY

NOHSC (1994) National Code of Practice for the Labelling of Workplace Substances [NOHSC:2012(1994)]. National Occupational Health and Safety Commission, Canberra, Australian Government Publishing Service.

NOHSC (2002) Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(2002)]. National Occupational Health and Safety Commission, Canberra, AusInfo.

NOHSC (2003) National Code of Practice for the Preparation of Material Safety Data Sheets, 2nd edn [NOHSC:2011(2003)]. National Occupational Health and Safety Commission, Canberra, Australian Government Publishing Service.