

File No: NA 915

April 2001

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

Polymer in Morfree 698A

This Assessment has been compiled in accordance with the provisions of the *Industrial Chemicals (Notification and Assessment) Act* 1989 (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 National Occupational Health and Safety Commission which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment and the assessment of public health is conducted by the Department of Health and Aged Care.

For the purposes of subsection 78(1) of the Act, copies of this full public report may be inspected by the public at the Library, National Occupational Health and Safety Commission, 92-94 Parramatta Road, Camperdown NSW 2050, between the following hours:

Monday - Wednesday	8.30 am - 5.00 pm
Thursday	8.30 am - 8.00 pm
Friday	8.30 am - 5.00 pm

Copies of this full public report may also be requested, free of charge, by contacting the Administration Coordinator on the fax number below.

For enquiries please contact the Administration Coordinator at:

Street Address: 92 -94 Parramatta Rd CAMPERDOWN NSW 2050, AUSTRALIA
Postal Address: GPO Box 58, SYDNEY NSW 2001, AUSTRALIA
Telephone: (61) (02) 9577 9514 FAX (61) (02) 9577 9465

Director
Chemicals Notification and Assessment

TABLE OF CONTENTS

FULL PUBLIC REPORT.....	3
1. APPLICANT	3
2. IDENTITY OF THE CHEMICAL.....	3
3. PHYSICAL AND CHEMICAL PROPERTIES	3
3.1 Comments on Physico-Chemical Properties	4
4. PURITY OF THE CHEMICAL.....	4
5. USE, VOLUME AND FORMULATION	5
6. OCCUPATIONAL EXPOSURE	5
7. PUBLIC EXPOSURE	6
8. ENVIRONMENTAL EXPOSURE.....	6
8.1 Release	6
8.2 Fate.....	7
9. EVALUATION OF TOXICOLOGICAL DATA	7
10. ASSESSMENT OF ENVIRONMENTAL EFFECTS	7
11. ASSESSMENT OF ENVIRONMENTAL HAZARD	7
12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS	8
13. RECOMMENDATIONS.....	9
14. MATERIAL SAFETY DATA SHEET	10
15. REQUIREMENTS FOR SECONDARY NOTIFICATION	10
16. REFERENCES.....	10

FULL PUBLIC REPORT**Polymer in Morfree 698A****1. APPLICANT**

Rohm and Haas Australia Pty Ltd of 4th Floor, 969 Burke Road, CAMBERWELL VIC 3124 (ACN 004 513 188) has submitted a limited notification statement in support of their application for an assessment certificate for Polymer in Morfree 698A.

2. IDENTITY OF THE CHEMICAL

The chemical name, other name, CAS number, molecular and structural formulae, molecular weight, spectral data, details of the polymer composition and details of exact import volume and customers have been exempted from publication in the Full Public Report and the Summary Report.

3. PHYSICAL AND CHEMICAL PROPERTIES

The physical properties listed are for the polymer solution (Morfree 698A product) unless otherwise stated.

Appearance at 20°C & 101.3 kPa:	Amber coloured solution
Boiling Point:	Not determined but expected to be high
Density:	<i>Ca.</i> 1100 kg cm ³
Vapour Pressure:	<0.1 x 10 ⁻⁴ kPa (20 °C) for 1,1'-methylenebis[4-isocyanatobenzene (MDI). see comments below.
Water Solubility:	<i>ca.</i> 8 mg/L - see comments below.
Partition Co-efficient (n-octanol/water):	Not determined -see comments below.
Adsorption/Desorption:	Not determined -see comments below.
Dissociation Constant:	Not determined. The polymer does not contain any groups which are expected to dissociate in water.
Flash Point:	218 °C; for MDI

Flammability Limits:	Non flammable; combustible
Autoignition Temperature:	Not expected to autoignite
Explosive Properties:	Not explosive
Reactivity/Stability:	The notified polymer contains unreacted isocyanate groups. The isocyanate groups will react with strong acids and alkali, alcohols, amines and water. Burning of the Morfree 698A product may produce nitrogen oxides, cyanide, carbon monoxide and carbon dioxide.

3.1 Comments on Physico-Chemical Properties

The vapour pressure provided relates to MDI. The vapour pressure of the notified polymer is likely to be low considering the high molecular weight of the polymer.

The water solubility was determined using a modified flask method (Pazdra 2000). Morfree 698A (*ca.* 5 g) was weighed into double filtered deionised water (50 mL, 0.2 micrometre filtered), the solution was shaken for 24 h and equilibrated for another 24 h. After equilibration, the sample was filtered (0.2 micrometre) and an aliquot was dried at 105 °C. The water solubility test was completed in triplicate and the average value was reported. This method indicated that the solubility of Morfree 698A is *ca.* 8 mg/L.

The notified polymer contains functional groups that may undergo reaction with water, suggesting that it will be slightly susceptible to hydrolysis. The remainder of the notified polymer contains linkages that are expected to undergo hydrolysis under extreme pH. However, in the environmental pH range of 4 to 9, significant hydrolysis of the linkages is unlikely to occur.

The partition coefficient has not been determined due to its expected low water solubility, and its likely hydrophobic nature, indicative of partitioning into the *n*-octanol phase. No adsorption/desorption tests were conducted for this notification. The notifier expects the notified polymer to be immobile in soil due to the high molecular weight, the monomer composition and the expected low water solubility.

The notified polymer contains terminal functional groups, classified as highly reactive functional groups. Nonetheless, the MSDS indicates that the polymer is stable under normal conditions.

4. PURITY OF THE CHEMICAL

Degree of Purity:	> 99 % w/w
Hazardous Impurities:	None
Non-hazardous Impurities (> 1% by weight):	None

Maximum Content of Residual Monomers:

All levels of residual monomers other than MDI are effectively zero as they would react with the excess MDI.

Additives/Adjuvants:

The product Morfree 698A contains an intentional excess of 2,4' and 4, 4'-diphenylmethane diisocyanate (MDI isomers).

<i>Chemical name:</i>	1,1'-methylenebis[isocyanatobenzene]
<i>Synonyms:</i>	Methylene bisphenyl isocyanate (MDI)
<i>CAS No.:</i>	26447-40-5
<i>Weight percentage:</i>	ca. 20-30 % w/w
<i>Toxic properties:</i>	Harmful by Inhalation (R20); Irritating to eyes, respiratory system and skin (R36/37/38); may cause sensitisation by inhalation (R42).

5. USE, VOLUME AND FORMULATION

The notified polymer will not be manufactured in Australia. It will be imported into Victoria as a component of Morfree 698A. The notified polymer will be used as one component of a "two pack" laminating adhesive for polymer and/or aluminium films used in snack food packaging and other general packaging.

Morfree 698A will be imported in 200 L steel drums and 20 L steel pails, with an estimated quantity of the notified polymer of *ca.* 10 tonnes in the first year increasing to 30 tonnes per annum after 5 years.

6. OCCUPATIONAL EXPOSURE

Transport and storage

The notifier has estimated that 5 waterside workers and 5-10 transport drivers and warehouse workers will be involved in the transport and storage of Morfree 698A. These workers could be exposed to the notified polymer only in the event of an accident where the packaging is breached. The product is not classified as Dangerous Goods in accordance with the Australian Code for the Transport of Dangerous Goods by Road and Rail.

Laminating machine operators

At the laminating site, the polymer in Morfree 698A is decanted by gravity from 200 L drums into a mixing vessel of 40-60 L capacity. It will be mixed mechanically with another component of the adhesive system in the mixing vessel. The blended adhesive containing 50-80 % notified polymer will be pumped mechanically from the mixing vessel to a holding vessel (*ca.* 20 L) of the laminating machine then pumped into an adhesive tray below the laminating machine rollers. The blended adhesive is applied by the gravure coating process where two polymers and/or aluminium film are laminated together with the adhesive between the films. Following completion of a run, unused adhesive in the laminating machine tray or reservoir is transferred to a waste drum manually. The adhesive residues on the machinery

are washed off manually using rags and ethyl acetate.

There will be 4-8 laminating machine operators who may be exposed to the product containing the notified polymer and the blended adhesive. The maximum potential exposure for laminating machine operators is estimated to be 6-8 hours per day, 50 days per year. The main routes for occupational exposure to the polymer may occur through dermal, eye and inhalation contact. Exposure to the notified polymer and MDI could be significant due to their high concentration. In addition, workers may be exposed to vapours of ethyl acetate. Laminating machinery operators will wear safety glasses, impervious gloves, overalls and safety boots during blending of the adhesive, transfer of the adhesive to laminating machines, and cleaning of the machines. Blending vessels are situated in a bunded area with local exhaust ventilation, while laminating machinery is either fitted with exhaust ventilation ducts above the adhesive tray or in a wall or ceiling adjacent to the machinery.

Workers at the packaging factories will handle the laminated material and packed dry food where the notified polymer is unavailable for absorption.

7. PUBLIC EXPOSURE

The notified polymer solution will not be sold to the public and will be used in laminate adhesive products for use in dry food and confectionery. The public will frequently handle packaging containing the notified polymer as a component of adhesive. However, since the notified polymer is "sandwiched" between two impervious polymer and/or aluminium films, food contact with the notified polymer is unlikely to occur.

8. ENVIRONMENTAL EXPOSURE

8.1 Release

During formulation of the adhesive and application, the notifier estimates that the usage rate of 30 tonnes per annum will generate up to 833 kg per annum of notified polymer waste. This will be derived from:

Spills: ≤ 150 kg/annum

Residues in the import containers: ≤ 111 kg/annum

Equipment cleaning: ≤ 52 kg/annum

Unused blend: ≤ 520 kg/annum

It is anticipated that spills of the polymer solution and blended polymer adhesive will be contained within the plant through the bunding systems in place. As the polymer solution will be used in small batch quantities, spills are expected to be relatively small in volume. Spills will be collected using absorbent material and removed by a licensed industrial waste contractor to a licensed waste landfill site.

Machinery will be manually cleaned with rags and solvent and waste from this process will be disposed to landfill by licensed hazardous waste contractors.

It is expected that empty import drums containing residual polymer solution will be used to collect waste solvent and unused blended adhesive, and removed by a licensed hazardous waste contractor. The liquid contents will be incinerated and the drums with any residual

solid will be disposed of to a licensed waste landfill site.

The remainder of the notified polymer will be incorporated into snack food or general packaging.

8.2 Fate

Spills of polymer solution or blended laminating adhesive containing the notified polymer will be collected on absorbent material and disposed of to landfill. Waste generated from cleaning machinery with rags and solvent, will also be disposed of to landfill. In landfill, the polymer is unlikely to separate from the absorbent material, but if so, would become associated with the soil matrix and not leach into the aquatic environment due to the expected low water solubility.

Residual polymer solution and unused blended adhesive will be incinerated by licensed hazardous waste contractors and the empty import drums with any remaining residual solid material, will be disposed of to landfill. Incineration would be expected to produce water vapour and oxides of nitrogen and carbon. In landfill, any polymer escaping from the drums would associate with the soil matrix and not leach into the aquatic compartment due to the expected low water solubility.

The majority of the notified polymer will follow the fate of snack food and general packaging in which it is incorporated. It is expected that the majority of packaging will be disposed of to domestic landfill. Upon eventual degradation of the packaging films between which the polymer is sandwiched, it is expected that the polymer would become part of the soil matrix and not be leach from the soil due to the low water solubility.

The polymer is not expected to cross biological membranes, due to its high molecular weight and predicted low water solubility, and should not bioaccumulate (Connell, 1990).

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data were submitted. However the Material Safety Data Sheet (MSDS) provided some summarised toxicological findings for MDI; MDI has a low acute oral toxicity $LD_{50} = 2200 \text{ mg/kg bw}$ in mouse, it may cause eye and skin and respiratory irritation, sensitisation by inhalation and nausea, vomiting and diarrhoea if ingested.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were submitted.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Release of the notified polymer to the aquatic environment from spills during formulation is not expected, as processing plants will be bunded and spills will be collected on absorbent material and disposed of to landfill. Waste polymer generated from cleaning equipment will be disposed of to landfill. The majority of the notified polymer will follow the fate of snack food and general packaging in which it is incorporated and eventually be disposed of to landfill. In landfill, the polymer is unlikely to be mobile in the soil environment and is

expected to very slowly degrade to carbon dioxide through abiotic and biotic processes. The environmental hazard of the notified polymer in landfill is expected to be low.

Incineration of the notified polymer in waste from drum residues and unused blended adhesive is expected to produce water vapour and oxides of carbon and nitrogen.

The polymer's high molecular weight and low water solubility should prevent bioaccumulation.

Given the above considerations, the overall environmental hazard is expected to be low.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

No toxicological data were provided for the notified polymer in Morfree 698A. However the MSDS summarised some toxicological findings for MDI; MDI has a low acute oral toxicity ($LD_{50} = 2200 \text{ mg/kg bw}$ in mouse), is expected to cause eye and skin irritation, sensitisation by inhalation and nausea, vomiting and diarrhoea if ingested. Due to its high NAMW, adsorption across biological membranes would be restricted.

An intentional excess of the hazardous monomer MDI is contained in the product, Morfree 698A, hence the product is classified as hazardous substance in accordance with the *NOHSC Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999), and carries the following risk phrases; Harmful by Inhalation (R20); Irritating to eyes, respiratory system and skin (R36/37/38); may cause sensitisation by inhalation (R42).

MDI has a national exposure standard (NOHSC, 1995; see below).

Occupational Health and Safety

Dermal and inhalational exposure to the polymer in Morfree 698A may occur during the blending and transfer of the blended adhesive, and when cleaning the laminating equipment. Exposure to high concentrations of MDI may also occur during these operations. Blending vessels are situated in a bunded area with local exhaust ventilation. Laminating machinery is either fitted with exhaust ventilation ducts above the adhesive tray, or in a wall or ceiling adjacent to the machinery.

Due to the health effects of MDI, the health risk to laminating operators is of concern, as exposure and therefore irritation of the skin and eyes, and sensitisation may occur during transfer and cleaning operations. Laminating machine operators must wear safety glasses, impervious gloves, overalls and safety boots when handling Morfree 698A and the blended adhesives. Respiratory protection must be worn if there is a risk of exposure to MDI. MDI has a NOHSC exposure standard of 0.02 mg/m^3 TWA (as isocyanate, equivalent to 0.12 mg/m^3 MDI) and 0.07 mg/m^3 STEL, with a 'sensitiser' notation. However, it is noted that the ACGIH TLV for MDI is 0.051 mg/m^3 TWA (ACGIH 2000)). Precautions to prevent exposure to isocyanates must be taken by all personnel, especially those who have had prior contact or suffer from any form of compromised respiratory function (NOHSC 1990). Isocyanates are on Schedule 3 in NOHSC Model Regulation for the Control of Workplace Hazardous Substances – substances for which health surveillance is required (NOHSC 1994a).

The notified polymer becomes unavailable for absorption once it is incorporated in the laminated material. The health risk for workers in the packaging industry, and in the distribution and retailing snack food and general goods is considered to be negligible.

There is little potential for significant health risk to the notified polymer in the transport and storage of the product containing this polymer, unless repeated accidental exposure occurs.

Public Health

The notified polymer is not available for sale to the public and will be used in laminate adhesive products for use in snack food and general packaging. Although members of the public may consume food from laminated packages manufactured using the notified polymer, the risk to public health from the notified polymer is likely to be low because it is sandwiched between two impermeable layers and is unlikely to be bioavailable.

13. RECOMMENDATIONS

Due to the presence of the residual monomer, MDI, which is a Schedule 3 sensitiser, health surveillance must be conducted for workers potentially exposed to Morfree 698A or mixtures containing the adhesive.

To minimise occupational exposure to Polymer in Morfree 698A, the following guidelines and precautions should be observed:

- Local exhaust ventilation in all areas where Morfree 698A and mixtures containing Morfree 698A are handled;
- Personal and area atmospheric monitoring should be conducted for workers potentially exposed to MDI in excess of the NOHSC exposure standard of 0.12 mg/m³ TWA.
- Workers must wear overalls, face/eye protection and rubber or neoprene gloves when handling Morfree 698A or mixtures containing the adhesive. Respiratory protection must be worn if exposure to MDI is possible;
- Spillage of the notified chemical should be avoided. Spillages should be cleaned up promptly with absorbents which should be put into containers for disposal;
- A copy of the MSDS should be easily accessible to employees.

If products containing the notified chemical are hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999), workplace practices and control procedures consistent with State and Territory hazardous substances regulations must be in operation.

Guidance in selection of goggles may be obtained from Australian Standard (AS) 1336 (Standards Australia, 1994) and Australian/New Zealand Standard (AS/NZS) 1337 (Standards Australia/Standards New Zealand, 1992); for industrial clothing, guidance may be found in AS 3765.2 (Standards Australia, 1990); for impermeable gloves or mittens, in AS

2161.2 (Standards Australia/ Standards New Zealand, 1998); for occupational footwear, in AS/NZS 2210 (Standards Australia/ Standards New Zealand, 1994a); for respirators, in AS/NZS 1715 (Standards Australia/ Standards New Zealand, 1994b) and AS/NZS 1716 (Standards Australia/ Standards New Zealand, 1994c) or other internationally acceptable standards.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the notified chemical was provided in a format consistent with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act, the director must be informed if any of the circumstances stipulated under subsection 64(2) of the Act arise, and secondary notification of the notified chemical may be required. No other specific conditions are prescribed.

16. REFERENCES

ACGIH (2000), 2000 TLVs and BEIs.

Connell D. W. (1990) General characteristics of organic compounds which exhibit bioaccumulation. In Connell D. W., (Ed) *Bioaccumulation of Xenobiotic Compounds*. CRC Press, Boca Raton, USA.

National Occupational Health and Safety Commission (1990) *Isocyanates*, Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1994a) *National Model Regulations for the Control of Workplace Hazardous Substances* [NOHSC: 1005 (1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1994b) *National Code of Practice for the Preparation of Material Safety Data Sheets* [NOHSC: 2011(1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1995) *Adopted National Exposure Standards for Atmospheric Contaminants in the Occupational Environment*, [NOHSC: 1003(1995)]. In: *Exposure Standards for Atmospheric Contaminants in the Occupational Environment: Guidance Note and National Exposure Standards*. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1999) Approved Criteria for Classifying Hazardous Substances [NOHSC: 1008 (1994)]. Australian Government Publishing Service, Canberra.

Pazdra, K. (2000). Solubles, Water, Woodstock Analytical Services.

Standards Australia (1990) Australian Standard 3765.2-1990, Clothing for Protection against Hazardous Chemicals Part 2 Limited protection against specific chemicals. Standards Association of Australia.

Standards Australia (1994) Australian Standard 1336-1994, Eye protection in the Industrial Environment. Standards Association of Australia.

Standards Australia/Standards New Zealand (1992) Australian/New Zealand Standard 1337-1992, Eye Protectors for Industrial Applications. Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1994) Australian/New Zealand Standard 2210-1994, Occupational Protective Footwear. Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1994) Australian/New Zealand Standard 1715-1994, Use and Maintenance of Respiratory Protective Devices. Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1994) Australian/New Zealand Standard 1716-1994, Respiratory Protective Devices. Standards Association of Australia/Standards Association of New Zealand.

Standards Australia/Standards New Zealand (1998) Australian/New Zealand Standard 2161.2-1998, Occupational protective gloves, Part 2: General requirements. Standards Association of Australia/Standards Association of New Zealand.