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# NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

#### **FULL PUBLIC REPORT**

# Polymer in Morfree 400A

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Director

Chemicals Notification and Assessment

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# **FULL PUBLIC REPORT**

### Polymer in Morfree 400A

# 1. APPLICANT

Rohm and Haas Australia Pty Ltd of Floor, 969 Burke Road Camberwell VIC 3124 (ACN 004 513 188) have submitted a limited notification statement in support of their application for an assessment certificate for Polymer in Morfree 400A.

#### 2. IDENTITY OF THE CHEMICAL

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

Marketing Name: Morfree 400A (75 % w/w notified polymer).

#### 3. PHYSICAL AND CHEMICAL PROPERTIES

The following physico-chemical data are from Morfree 400A polymer solution in 1,1'-methylenebis[isocyanatobenzene] (MDI), unless otherwise stated.

Appearance at 20°C & 101.3 kPa: amber liquid

**Boiling Point:** not determined

Specific Gravity: 1.1

**Vapour Pressure:** the notified polymer is not volatile

Water Solubility: 36 mg/L

**Partition Co-efficient** 

(n-octanol/water): not determined (see comments below)

Hydrolysis as a Function of pH: the polymer linkages may undergo hydrolysis under

extreme temperature and pH

Adsorption/Desorption: not determined (see comments below)

**Dissociation Constant:** no dissociable groups are present

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Particle Size: not applicable as the notified polymer is only used in

solution

Flash Point: 218°C (closed cup) (MDI)

Flammability Limits: not determined

**Autoignition Temperature:** not determined (see comments below)

**Explosive Properties:** not explosive

**Reactivity/Stability:** the notified polymer contains isocyanate groups which

will react with acids, bases, amines, alcohols and water

# 3.1 Comments on Physico-Chemical Properties

The water solubility was determined using a modified flask method (Pazdra 2001). The notified polymer ( $\sim$ 0.5 g) was weighed into double filtered deionised water (50 mL, Millipore water filtered through a 0.2  $\mu$ m filter), the solution was shaken for 24 h and equilibrated for another 24 h. After equilibration, the sample was filtered and an aliquot was dried at 105°C. The water solubility test was completed in triplicate and the average value was reported.

The terminal isocyanate groups are expected to hydrolyse on contact with water. The notified polymer also contains linkages that may undergo hydrolysis, but this is unlikely in the environmental pH range 4-9.

The partition coefficient has not been determined in consideration of its low water solubility and likely hydrophobic nature, which indicates that partitioning into the n-octanol phase is likely.

The adsorption/desorption was not determined, but the notifier has indicated that the polymer is expected to be immobile in soil due to its composition, low water solubility and high molecular weight.

No flammability properties for the notified polymer have been determined; however the notified polymer is expected to be combustible. The polymer solution is not a flammable liquid due to the low vapour pressure of MDI.

The polymer is expected to remain stable under ambient conditions, except for reactions of the terminal isocyanate groups. The notified polymer is designed to cross-link with other polymers via these isocyanate groups.

#### 4. PURITY OF THE CHEMICAL

**Degree of Purity:** 70 - 80 %

# Additives/Adjuvants:

Chemical name: 1,1'-methylenebis[isocyanatobenzene]

Synonyms: MDI

*CAS No.*: 26447-40-5 *Weight percentage*: 24 - 26 %

Toxic properties: R20 Harmful by inhalation

R36/37/38 Irritating to eyes, respiratory system and

skin

R42 May cause sensitisation by inhalation (NOHSC,

1999a)

NOHSC exposure standard 0.02 mg/m<sup>3</sup> TWA as

isocyanate (NOHSC, 1995)

# 5. USE, VOLUME AND FORMULATION

The notified polymer is used as one component of a two pack laminating adhesive for plastic and/or aluminium films used to package dry food and in general packaging.

The notified polymer will not be manufactured in Australia, but will be imported as a component in the product, Morfree 400A. The estimated import quantity of the notified polymer is less than 10 tonnes per annum during the first five years.

Morfree 400A is a solution containing 75 % notified polymer in MDI. This will be blended prior to use to produce an adhesive formulation which consists predominantly of Morfree 400A. Morfree 400A will be imported in 200 L steel drums.

#### 6. OCCUPATIONAL EXPOSURE

#### Transport and storage

The notifier estimated that 5 waterside workers and 5-10 transport drivers and warehouse workers will be involved in the transport and storage of the product containing the notified polymer. These workers could be exposed to the notified chemical only in the event of an accident where the packaging is breached.

# Laminating machine operator

At the laminating site, Morfree 400A is transferred by gravity through an attached tap from 200 L drums into a mixing vessel of 40-60 L capacity. It will be mixed with another component of the adhesive system in the mixing vessel mechanically for 15 minutes. The blended adhesive containing < 50 % notified polymer is pumped mechanically from the mixing vessel to a holding vessel (about 20 L) of the laminating machine and further pumped to an adhesive tray. 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, 30 days per year. The main routes for occupational exposure to the polymer will occur through skin and eye contact. Contact with the notified polymer is possible during blending and transfer of adhesives, and during cleaning. Laminating machinery operators 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.

There is little potential for exposure to the notified polymer after it has been incorporated in packaging materials, because it will be sandwiched between two impervious layers and also crosslinked and not separately available for exposure.

# 7. PUBLIC EXPOSURE

The notified polymer is not available for sale to the public and will be used as an ingredient in laminating adhesive products for use in food and other packaging applications. The potential for public exposure to the notified polymer during transport, reformulation or disposal is likely to be low. There is little potential for exposure of the public to the notified polymer in packaging materials, because it will be sandwiched between two impervious layers and also crosslinked and not separately available for exposure.

# 8. ENVIRONMENTAL EXPOSURE

#### 8.1 Release

The notifier has estimated the following amounts of the polymer solutions may be lost from the sources specified as a result of the formation and use of the adhesive:

Spills:  $\leq 76 \text{ kg per annum}$ Residues in the import containers:  $\leq 19 \text{ kg per annum}$ Equipment cleaning:  $\leq 15 \text{ kg per annum}$ Unused blend:  $\leq 150 \text{ kg per annum}$ 

The total amount of notified polymer that may be wasted during its use is likely to be less than 260 kg/year when 5 tonnes of Morfree 400A are imported.

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, it is expected that any spills will be 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 of to landfill by licensed hazardous waste contractors.

It is expected that import drums containing residual polymer solution will be used to collect waste solvent and unused blended adhesive, and when finished with, collected 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 packaging materials.

#### **8.2** Fate

Spills of polymer solution or blended laminating adhesive containing the notified polymer will be collected on absorbent material and disposed of in landfill. Waste generated from cleaning machinery with rags and solvent will also be disposed of in landfill. In landfill, the polymer is unlikely to separate from the absorbent material; any free polymer would associate with the soil matrix and not leach into the aquatic compartment due to the low water solubility of the notified polymer.

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 in landfill. Incineration would be expected to produce water vapour and oxides of nitrogen and carbon. In landfill, the polymer would not be expected to escape from the drums; any free polymer would associate with the soil matrix and not leach into the aquatic compartment due to its low water solubility. The majority of the notified polymer will follow the fate of the packaging in which it is incorporated. It is expected that the majority of packaging will be disposed of in 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 leached from the soil due to its low water solubility.

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

#### 9. EVALUATION OF TOXICOLOGICAL DATA

No toxicology data were submitted. The notified polymer contains reactive isocyanate functional groups which can cause local irritant and allergic reactions (NOHSC, 1990).

#### 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicity data were submitted.

#### 11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Release of the notified polymer to the aquatic compartment from spills during formulation is not expected, as processing plants will be bunded and any spills will be collected on absorbent material and disposed of in landfill. Waste polymer generated from cleaning equipment and discarded packaging will be disposed of in landfill. In landfill, the polymer is unlikely to be mobile in the soil environment and is expected to very slowly degrade to gases such as carbon dioxide through abiotic and biotic processes. The environmental hazard of the notified polymer in landfill is expected to be low.

Incineration by licensed hazardous waste contractors of the notified polymer in waste from drum residues and unused blended adhesive would be expected to produce water vapour and oxides of carbon and nitrogen.

The high molecular weight of the notified polymer should prevent bioaccumulation. The overall environmental hazard is therefore expected to be low.

# 12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

No toxicological information has been provided for the notified polymer. Any toxicological studies on the notified polymer would be influenced by the effects of the added 1,1'-methylenebis[isocyanatobenzene] (MDI) and therefore it is not appropriate to classify the notified polymer against the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b). Since the notified polymer has high NAMW, absorption across biological membranes and resultant systemic toxicity would be restricted. However, it contains reactive isocyanate functional groups which can cause local irritant and allergic reactions (NOHSC, 1990). The product Morfree 400A contains an excess of MDI, which is on the NOHSC *List of Designated Hazardous Substances* (NOHSC, 1999a) as a respiratory sensitiser and skin, eye and respiratory irritant. The product Morfree 400A is classified as a hazardous substance on the basis of the presence of the high level of MDI, and given risk phrases: R20 - Harmful by inhalation; R36/37/38 - irritating to eyes, respiratory system and skin; R42 - may cause sensitisation by inhalation.

The MSDS for Morfree 400A lists a large number of potential health effects, relating chiefly to the hazards associated with the isocyanate groups of the notified polymer and the excess MDI.

# Occupational health and safety

There is little potential for significant health risk to the notified polymer in the transport and storage of the product containing this polymer.

Potential exposure to the polymer in Morfree 400A will be during the blending and transfer of adhesives, particularly manual transfer, and when cleaning equipment. Exposure to the notified polymer *via* inhalation is expected to be minimal due to its low volatility. Inhalation exposure to the product should however be stringently controlled due to the hazard associated with the excess of MDI. Exposure to the notified polymer is most likely to be by skin contact. However, laminating machine operators are instructed to wear safety glasses, impervious gloves (nitrile or butyl rubber), overalls and safety boots when handling Morfree 400A and the blended adhesives. In addition, 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 400A and the blended adhesives and respiratory protection must be worn if there is a risk of exposure to MDI. MDI has a NOHSC exposure standard of 0.02 mg/m³ TWA (as isocyanate, equivalent to 0.12 mg/m³ MDI) and 0.07 mg/m³ STEL, with a 'sensitiser' notation (NOHSC, 1995). However, it is noted that the ACGIH TLV for MDI is 0.051 mg/m³ TWA (American Conference of Government Industrial Hygienists, 1998)). 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 Regulations 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 distribution and retailing, is considered to be negligible.

#### Public health

It is expected that public exposure to the notified polymer in its liquid state will be limited, except in the rare event of an accidental spill. The notified polymer used in an adhesive in food and other packaging will be encapsulated within an inert, very high molecular weight film matrix, rendering the notified polymer biologically unavailable. Public contact with the notified polymer in packaging is further limited as the adhesive containing the notified polymer is sandwiched between two layers of polymer and/or aluminium film, restricting any dermal contact. Consequently the public hazard from exposure to the notified polymer through all phases of its life cycle, is considered to be low.

#### 13. RECOMMENDATIONS

Due to the presence of excess MDI, which is a Schedule 3 sensitiser, health surveillance must be conducted for workers potentially exposed to Morfree 400A or mixtures containing the adhesive.

To minimise occupational exposure to Polymer in Morfree 400A the following guidelines and precautions should be observed:

- Local exhaust ventilation should be used in all areas where Morfree 400A and mixtures containing Morfree 400A 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/m<sup>3</sup> TWA. Employers should ensure that other relevant NOHSC exposure standards are not exceeded in the workplace;

- Workers must wear overalls, face/eye protection and butyl rubber or nitrile gloves when handling Morfree 400A 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 polymer are hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999b), 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 2919 (Standards Australia, 1987) and AS 3765.2 (Standards Australia, 1990); for impermeable gloves or mittens, in AS 2161 (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, 1994b) and AS/NZS 1716 (Standards Australia/ Standards New Zealand, 1994c) and other internationally acceptable standards.

#### 14. MATERIAL SAFETY DATA SHEET

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

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

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Pazdra, K (2001): Sample Report; Submission No. 200001157: Project Number 981109-60922041: Woodstock Analytical Services (unpublished report).

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