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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polymer in Morfree 406LV

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Director Chemicals Notification and Assessment

FULL PUBLIC REPORT

Polymer in Morfree 406LV

1. APPLICANT

Coates Australia Pty Ltd (ACN 000 079 550) of 323 Chisholm Rd AUBURN NSW 2144 and Rohm and Haas Australia Pty Ltd (ACN 004 513 188) of 969 Burke Rd CAMBERWELL VIC 3124 have submitted a limited notification statement in support of their application for an assessment certificate for Polymer in Morfree 406LV.

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 purity have been exempted from publication in the Full Public Report and the Summary Report.

Marketing Name: Morfree 406LV (contains notified polymer including

20-30% intentional excess of 1,1'-

methylenebis[isocyanatobenzene])

Molecular Weight:

Number-Average > 1 000

Molecular Weight (NAMW):

Weight-Average > 1 000

Molecular Weight:

Maximum Percentage of Low Molecular Weight Species

Molecular Weight < 500: < 5% **Molecular Weight < 1 000:** < 17%

Method of Detection and Gel Permeation Chromatography and Infrared

Determination: spectroscopy.

Spectral Data: An infrared spectrum was provided for Morfree 406LV.

3. PHYSICAL AND CHEMICAL PROPERTIES

The physico-chemical properties is for Morfree 406LV unless otherwise stated.

Appearance at 20°C & 101.3 kPa: Amber viscous liquid.

Boiling Point: > 200°C

Specific Gravity: 1.21

Vapour Pressure: 10.1 kPa at 20°C (see comments below).

Water Solubility: The notified polymer is expected to have low water

solubility due to its high molecular weight, the high proportion of hydrophobic monomers and reaction of

NCO groups with water.

Partition Coefficient: The partition coefficient has not been determined due to

the reaction of NCO groups with water.

Hydrolysis as a function of pH: The notified polymer contains urethane groups that may

undergo hydrolysis under extremes of pH and

temperature.

Adsorption/Desorption: Not determined.

Dissociation Constant: The notified polymer does not contain any groups

which can undergo dissociation.

Particle Size: Not applicable.

Flash Point: > 200°C.

Flammability Limits: Not applicable.

Autoignition Temperature: > 400°C.

Explosive Properties: The notified polymer is stable and not explosive under

normal conditions.

Reactivity/Stability: Reacts with water and urethane groups may undergo

hydrolysis under extreme temperature and pH.

3.1 Comments on Physico-Chemical Properties

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

Although no water solubility data are provided, the notifier expects the solubility of the notified polymer to be insignificant due to the high molecular weight and the high proportion of hydrophobic monomers. Water solubility would be difficult to measure due to the presence of isocyanate groups.

The notified polymer contains terminal isocyanate groups that may react with water suggesting that the notified polymer will be susceptible to hydrolysis. The remainder of the notified polymer contains urethane and ester linkages that could be expected to undergo hydrolysis under extreme pH. However, as the notified polymer is formulated at mild pH significant hydrolysis of the urethane and ester linkages is unlikely.

The partition coefficient has not been determined due to the reaction of isocyanate groups with water. The partition coefficient of the notified polymer is expected to be high due to its expected low water solubility and likely hydrophobic nature.

No adsorption/desorption tests were conducted. 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.

Although no dissociation tests were conducted, the notifier expects that the notified polymer will not undergo dissociation as there are no functional groups which can dissociate.

The notified polymer contains terminal isocyanate groups, which are classified as highly reactive functional groups. Nonetheless, the Material Safety Data Sheet (MSDS) indicates that the polymer is stable under normal conditions.

4. PURITY OF THE CHEMICAL

Degree of Purity: Very high.

Hazardous Impurities: Residual monomers some of which may be hazardous

are present at a combined concentration of less than

1%.

Non-hazardous Impurities

(> 1% by weight):

None.

Maximum Content of

Residual Monomers:

1%

Additives/Adjuvants:

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

Synonyms: Diphenylmethane diisocyanate

CAS No.: 26447-40-5

Weight percentage: 20-30%

Toxic Properties: 1,1'-methylenebis[isocyanatobenzene] is not

specifically listed on the *NOHSC List of Designated Hazardous Substances*. However, 4-4'-MDI is classified as harmful by inhalation, irritating to eyes, respiratory system and skin and sensitising by inhalation at concentrations equal to or greater than 25% (National Occupational Health and Safety Commission, 1999a). The NOHSC exposure standard for isocyanates is 0.02 mg/m³ (TWA) and 0.07 mg/m³ (as –NCO) (National Occupational Health and Safety

Commission, 1995).

5. USE, VOLUME AND FORMULATION

The notified polymer is to be used as a component of a two pack laminating adhesive for polymer and/or aluminium films for snack foods (eg potato crisps) and other general packaging. It is imported in 200 L steel drums and 20 L steel pails in a formulation with an intentional excess of 1,1'-methylenebis[isocyanatobenzene] (20-30%). The volume to be imported is 15 tonnes in the first year increasing to 40 tonnes per year by the fifth year.

6. OCCUPATIONAL EXPOSURE

Five waterside workers and 10 - 20 transport drivers and warehouse workers will be involved in transport and storage. Exposure will occur only in the event of accidental spillage.

Ten to twenty laminating machinery operators working for 6 – 8 hours/day, 100 days per year are involved in mixing adhesive and operation of the laminating machinery containing the mixed adhesive. The product, Morfree 406LV, is decanted from the 200 L drums through an attached tap by gravity feed or manually poured into 20 - 50 L steel vessels. Inhalation exposure to the notified polymer is unlikely due to its expected low vapour pressure and the presence local exhaust ventilation over the storage and mixing vessels and laminating machinery. Following addition to the steel vessels, the two parts of the adhesive are pumped through separate hoses to a mixing nozzle where the components are mixed. The blended adhesive is pumped mechanically from the mixing vessel to a 20 L holding vessel on the laminating machine and to the adhesive tray. The adhesive is applied to rollers and to aluminium or polymer films to be laminated together. Dermal exposure and eye contact is possible during addition of the notified polymer to the steel holding vessels by decanting or pouring and during cleaning of the laminating machinery. Cleaning of the machinery involves manual transfer of unused adhesive from the laminating machine tray or reservoir to a waste adhesive and solvent drum and washing off residue with rags and solvent ethyl acetate. The workers wear safety glasses, impervious gloves, overalls and safety boots to control exposure.

Although workers at factories will handle packaging material manufactured using the notified polymer, there is little potential for exposure as the adhesive containing the polymer is between two impervious films.

7. PUBLIC EXPOSURE

Polymer in Morfree 406LV will not be sold to the general public. During transportation, the public could only be exposed to the notified polymer in the event of an accidental spill. Although the public will handle packaging manufactured using the notified polymer, there is little potential for exposure as the adhesive containing the polymer is tightly held between two impervious films within the cured polymer matrix.

8. ENVIRONMENTAL EXPOSURE

8.1 Release

During formulation of the notified polymer, the notifier estimates that up to 375 kg/annum in year 1, increasing to 1000 kg/annum in year 5, of waste will be generated. This will be derived from:

Spills: 75–200 kg/annum (0.5%); Residues in the import containers: 150–400 kg/annum (1%); Equipment cleaning: 150–400 kg/annum (2%).

Any unused blended adhesive on the blending equipment, adhesive trays and laminating machinery is manually transferred to a waste adhesive and solvent drum or wiped up using rags and ethyl acetate. The polymer waste from the above processes will be collected in the empty import drums and disposed of to landfill by licensed hazardous waste contractors.

The remainder of the notified polymer, up to 14.6–39.0 tonnes/annum, will have been incorporated into the snack food and other packaging.

8.2 Fate

Notified polymer spilt or wasted during the formulation process will be disposed of to landfill by licensed hazardous waste contractors in the steel importation drums. In landfill, the polymer is likely to associate with the soil matrix and is not expected to leach into the aquatic environment. The notified polymer would be expected to slowly degrade to gases such as oxides of carbon and nitrogen through abiotic and biotic processes. If incinerated, the notified polymer wastes would be rapidly destroyed and converted to water vapour and oxides of carbon and nitrogen.

The majority of the notified polymer will be contained in snack food and other packaging, and ultimately make its way into domestic landfill as household garbage. Upon eventual degradation of the packaging films it is likely that the resulting end polymer would become part of the soil matrix and not leach from the soil by water because of the high molecular weight and hydrophobicity.

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

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data were provided.

The notified polymer is not classified as a hazardous substance according to the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999). It contains low level of residual monomers.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No toxicological data were provided

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Minimal release to the aquatic environment is expected during the use of the notified polymer in the formulation of the laminated adhesive. Small quantities of the notified polymer, derived from either spills or residue waste, will ultimately be released to landfill. In the event of a leak in the landfill, the polymer is unlikely to be mobile in the soil environment. The environmental hazard of the notified polymer in landfill is expected to be low. If incinerated, the polymer would be rapidly destroyed and converted to water vapour and oxides of carbon and nitrogen.

Minimal release to the aquatic environment is expected through the disposal of snack food packaging to domestic landfill. As the packaging gradually degrades the resulting end polymer is likely to become part of the soil matrix and not leach into the aquatic environment because of the high molecular weight and hydrophobicity.

The low molecular weight fragments (up to 17% below MW 1000, equating to approximately 2.6–6.8 tonnes depending on import volume) are not likely to pose a significant environmental hazard as they are likely react with the hydroxylated polyester resin and associate with the polymer matrix.

In the event of accidental release of the notified polymer into soils or waterways, the correct MSDS procedures should be followed.

The polymer's high molecular weight and expected 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

Hazard Assessment

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] 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 Morefree 406LV, contains an excess (20-30%) of 1,1'-methylenebis[isocyanatobenzene]. A different isomer of MDI, 4,4-MDI, is on the NOHSC *List of Designated Hazardous Substances* (NOHSC, 1999a) and described as harmful by inhalation, a respiratory sensitiser and skin, eye and respiratory irritant. The product Morefree 406LV is therefore classified as a hazardous substance, and given risk phrases: R20: Harmful by inhalation; R36/37/38: Irritating to eyes, respiratory system and skin and R42: May cause sensitisation by inhalation.

Occupational Health and Safety

The polymer solution is transported in 20 L and 200 L steel containers. Exposure of transport and storage workers is only possible in the event of accidental spillage.

The two parts of the adhesive which will contain the notified polymer are added to holding vessels connected to a mixing nozzle and a 20 L adhesive holding tank attached to a The most likely points at which exposure may occur are during laminating machine. decanting of imported polymer solution to its holding vessel and during clean-up of the laminating machine. Workers will not be exposed during transfers and lamination of films as the system is automatic and fitted with local exhaust ventilation over the storage and mixing vessels and the laminating machinery. However, inhalation exposure to the notified polymer will not occur because of its expected negligible vapour pressure. Dermal and ocular exposure is possible if there are spills during decanting and particularly during cleaning up the machinery with rags and solvent. To control exposure, workers will need to wear safety glasses, rubber or neoprene gloves (as specified in the MSDS), overalls and safety boots. The 1,1'-methylenebis[isocyanatobenzene] content of the imported polymer solution presents a risk of toxic effects via inhalation, irritation to skin, eyes and respiratory system and respiratory sensitisation. It is the employer's responsibility to maintain atmospheric levels of 1,1'-methylenebis[isocyanatobenzene] below the NOHSC exposure standard of 0.02 mg/m³ (TWA) and 0.07 mg/m³ STEL (as -NCO) (National Occupational Health and Safety Commission, 1995 equivalent to 0.12 mg/m³ MDI). However, it is noted that the ACGIH TLV for MDI is 0.051 mg/m³ TWA (ACGIH 2000). The risk of occupational asthma from repetitive exposure to isocyanates is well known. Therefore, respiratory protection during decanting and machine clean-up is indicated. The use of self-contained breathing apparatus should be considered to prevent worker exposure. Given the sensitising properties of isocyanates, precautions to prevent exposure must be taken by all personnel, but especially those who either have had prior contact with isocyanates or suffer from any form of compromised respiratory function (NOHSC Worksafe Australia Guide - Isocyanates; National Occupational Health and Safety Commission, 1990). Health surveillance for

isocyanates should be conducted (National Occupational Health and Safety Commission, 1994a).

Public Health

Public exposure to the notified polymer is unlikely during transport, storage or use. Although members of the public may consume food from laminated packages manufactured using the notified polymer, the risk to public health is likely to be low because it is sandwiched between two impervious layers and is unlikely to be bioavailable.

13. RECOMMENDATIONS

To minimise occupational exposure to the notified polymer the following guidelines and precautions should be observed:

- Spillage of the notified chemical should be avoided. Spillage 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 (National Occupational Health and Safety Commission, 1999b), workplace practices and control procedures consistent with State and Territory hazardous substances regulations must be in operation.

For products and formulations containing free 1,1'-methylenebis[isocyanatobenzene] the following guidelines and precautions should be observed:

- Local exhaust ventilation in all areas where products containing the notified polymer are handled;
- Personal and area atmospheric monitoring should be conducted for workers potentially exposed to 1,1'-methylenebis[isocyanatobenzene] in excess of the NOHSC exposure standard of 0.02 mg/m³ TWA. Employers should ensure that other relevant NOHSC exposure standards are not exceeded in the workplace;
- Workers must wear overalls, face/eye protection and rubber or neoprene gloves when handling products containing the notified polymer. Respiratory protection must be worn if exposure to 1,1'-methylenebis[isocyanatobenzene] is possible;
- 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/NZS 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 accepted standards.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the product containing the notified chemical was provided in a format consistent with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (National Occupational Health and Safety Commission, 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

ACGIH (2000). 2000 TLV and BEIs

Connell, D.W. (1990). General Characteristics of Organic Compounds Which Exhibit Bioaccumulation. In: Bioaccumulation of Xenobiotic Compounds, pp. 47-57. CRC Press, Boca Raton, USA.

National Occupational Health and Safety Commission (1990) Worksafe Australia Guide - Isocyanates. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1994a) National Model Regulations for 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 (1999a) List of Designated Hazardous Substances [NOHSC:10005(1999)]. Australian Government Publishing Service, Canberra.

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

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

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

Standards Australia/Standards New Zealand (1995a) Australian/New Zealand Standard 4114.1-1995, Spray painting booths - Design, construction and testing. Standards Association of Australia/Standards Association of New Zealand, Sydney/Wellington.