

June 2001

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

Polymer in Witcothane EAP 2000D

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Director
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FULL PUBLIC REPORT**Polymer in Witcothane EAP 2000D****1. APPLICANT**

Uniroyal Chemical Pty Ltd (ACN 005 225 507) of Unit 2, 13 Stanton Road SEVEN HILLS NSW 2147 has submitted a limited notification statement in support of their application for an assessment certificate for "Polymer in Witcothane EAP 2000D".

2. IDENTITY OF THE CHEMICAL

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

Other Names: NCO terminated polyester

Marketing Name: Witcothane EAP 2000D (containing 30-60% notified polymer)

3. PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical data were determined from the polymer solution Witcothane EAP 2000D containing 30-60% notified polymer in 1,1'-methylenebis[4-isocyanatobenzene] (MDI), unless otherwise stated.

Appearance at 20°C & 101.3 kPa: Viscous liquid

Boiling Point: > 200°C

Specific Gravity: 1.17

Vapour Pressure: The high molecular weight of the notified polymer indicates low volatility.

Water Solubility: The notified polymer will react with water to form an insoluble urea-capped polyester and CO₂.

Partition Co-efficient (n-octanol/water): Not determined as the notified polymer will react with water.

Hydrolysis as a Function of pH: The notified polymer contains isocyanate groups that

will react with water. The ester linkages in the polymer backbone are expected to be resistant to hydrolysis under normal conditions.

Adsorption/Desorption:	Not determined. The notified polymer is expected to be immobile in soil, reacting with moisture to form a very stable insoluble urea capped polyester.
Dissociation Constant:	The polymer does not contain any groups which can undergo dissociation.
Particle Size:	Not determined for the polymer solution.
Flash Point:	> 200°C
Flammability Limits:	Not determined
Autoignition Temperature:	Not determined
Explosive Properties:	The notified polymer is stable and is not explosive. However, the free MDI will react with water to release CO ₂ (causing pressure build-up)
Reactivity/Stability:	Notified polymer contains unreacted isocyanate groups (see comments below).

3.1 Comments on Physico-Chemical Properties

The notified polymer contains urethane linkages that could be expected to undergo hydrolysis under extreme pH.

The notified polymer is hydrophobic and likely to partition into the octanol phase.

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

4. PURITY OF THE CHEMICAL

Hazardous Impurities:

<i>Chemical name:</i>	MDI homopolymer
<i>CAS No.:</i>	Not provided.
<i>Weight percentage:</i>	1.2%
<i>Toxic properties:</i>	MDI is on the NOHSC Hazardous Substance List with R42 (May cause sensitisation by inhalation) when present at 1-5% (NOHSC, 1999a). The NOHSC

exposure standard for isocyanates is 0.02 mg/m³ (TWA) and 0.07 mg/m³ (as –NCO) (NOHSC, 1995).

**Non-hazardous Impurities
(> 1% by weight):**

None

**Maximum Content of Residual
Monomers and Additives:**

MDI is both a monomer and added at an intentional excess of 45% during polymer synthesis.

<i>Chemical name:</i>	1,1'-Methylenebis[4-isocyanatobenzene]
<i>Synonyms:</i>	Methylene bisphenyl isocyanate; MDI.
<i>CAS No.:</i>	101-68-8
<i>Weight percentage:</i>	45%
<i>Toxic Properties:</i>	On the NOHSC Hazardous Substance List. At ≥25% it requires R20 (Harmful by inhalation), R36/37/38 (Irritating to eyes, respiratory system and skin) and R42 (May cause sensitisation by inhalation) (NOHSC, 1999a). The NOHSC exposure standard for isocyanates is 0.02 mg/m ³ (TWA) and 0.07 mg/m ³ (as –NCO) (NOHSC, 1995).

Loss of monomers/additives/impurities is possible, but once the polymer is cured, all ingredients are trapped within the polymer matrix.

5. USE, VOLUME AND FORMULATION

The notified polymer will be synthesised in Australia and used in the manufacture of moulded shoe soles. Between 200 to 250 tonnes of the notified polymer will be manufactured annually. After manufacturing, the polymer solution, Witcothane EAP 2000D containing approximately 50% of the notified polymer, will be packaged in 1 000 kg IBC and sent to a separate factory for moulding.

6. OCCUPATIONAL EXPOSURE

Manufacturing site

There will be one manufacturing site synthesising the notified polymer in Australia. Exposure data are summarised in the following table.

<i>Category of worker</i>	<i>Number of worker</i>	<i>Max. exposure (hrs/day)</i>	<i>Max. exposure (days/yr)</i>
Kettle operator	1	7	52
Quality control	1	6	52

Witcothane EAP 2000D is synthesised in a vacuum mixing tank. All ingredients including the excess of MDI are directly loaded from drums into the mixing tank via a suction pipe. Each batch consists of 4-5 tonnes of the notified polymer and is produced over a 6 hour cycle. After synthesis, Witcothane EAP 2000D is transferred into 1 000 kg bulk containers, under a blanket of nitrogen gas and transported to a separate site for the manufacture of shoe soles.

Exposure to the monomers and notified polymer during manufacturing would most likely occur through incidental skin and eye contact. There is little potential for inhalation exposure due to the low volatility of the notified polymer and the use of a closed system.

A fully operational air exhaust system is in place to remove fumes. Workers at manufacturing site wear gloves, overalls and full-face respirators.

Transport

Transport workers are unlikely to experience any occupational exposure to the notified polymer in IBC unless the packaging was breached.

Moulding site

There is one moulding site in Australia. The injection machine operators will receive Witcothane EAP 2000D in 1 000 kg IBCs and connect them to injection machines via a permanent enclosed hose. All the injection machines are operated automatically.

<i>Category of worker</i>	<i>Number of worker</i>	<i>Max. exposure (hrs/day)</i>	<i>Max. exposure (days/yr)</i>
Injection machine operator	4	8	200

Exposure to the notified polymer during the moulding process may occur through incidental skin and eye contact when connecting and disconnecting the hose, and during cleaning and repairing equipment. Inhalation exposure is unlikely due to the low volatility of the notified polymer. As the moulding process is fully automated, workers are unlikely to be exposed to the mould mix during this process. Following moulding, the notified polymer is trapped within a matrix and becomes unavailable for exposure or absorption.

Extraction ports are fitted over the injection area to remove vapours. Workers will wear gloves, protective clothing and safety goggles.

7. PUBLIC EXPOSURE

There is the potential for exposure to the public should a spill occur during transport. The MSDS recommends the procedures for containing and cleaning up of liquid spills.

Public exposure will occur with contact with finished shoe soles, however this is likely to give very little exposure as the polymer is trapped within a matrix.

8. ENVIRONMENTAL EXPOSURE

8.1 Release

The notifier estimates that during manufacture, up to 50 kg per annum of notified polymer waste will be generated. These wastes will result from reactor kettle draining and small spills and will be disposed of in landfill. The shoe sole injection machines will operate on a continuous basis with no cleaning between shifts. Any excess polymer formulation that results from the moulding process will be air cured to form the corresponding urea capped polyester, and collected and disposed of in landfill by a licensed waste disposal contractor. Empty IBCs will be returned to the manufacturer and refilled with the notified polymer without rinsing.

The majority of the notified polymer will be incorporated into footwear.

8.2 Fate

Spills and wastes from the manufacturing process will be allowed to air cure prior to being collected and disposed of in landfill. The notified polymer reacts with water in the air to form a stable urea capped polyester. Waste generated from the cleaning of machinery will also be disposed of in landfill. In landfill, the notified polymer will react with water to form a stable insoluble urea capped polyester, expected to associate with the soil matrix and not leach into the aquatic compartment.

The majority of the notified polymer will follow the fate of footwear in which it is incorporated, most of which will be disposed of in domestic landfill. Upon eventual degradation of the footwear, it is expected that the polymer would become part of the soil matrix and not leach from the soil because of the expected low water solubility.

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

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data provided for assessment.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data provided for assessment.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Release of the notified polymer to the aquatic environment from spills during manufacture and automated shoe sole moulding is not expected, as any spills will be collected and disposed of in landfill. Waste polymer generated from cleaning equipment will be disposed of in landfill. The majority of the notified polymer will follow the fate of the footwear and eventually be disposed of in landfill. In landfill, the polymer will exist as a stable urea capped polyester. It 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.

The polymer's large 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 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 limited.

The polymer solution containing MDI at 30-60% is a hazardous substance and warrants the health effects classification R20, R36/37/38, R42. There is a NOHSC exposure standard for MDI.

The MSDS for Witcothane EAP 2000D indicates potential health effects including moderately toxic after ingestion, irritating to eyes, skin and respiratory system. Chronic skin contact with Witcothane EAP 2000D may cause an allergic reaction and repeated inhalation may cause respiratory sensitisation and asthma. Individuals with underlying lung disease may become more susceptible to these effects. These effects are expected to be due to the MDI rather than the notified polymer.

Occupational Health and Safety

There will be one manufacturing site in Australia. The notified polymer will be synthesised in a closed system with an air exhaust system to remove any fumes. All ingredients are loaded mechanically. The most likely points at which exposure may occur are during connecting and disconnecting the suction pipes, through incidental skin and eye contact. Inhalation exposure is unlikely to the notified polymer. The notifier states that workers at the manufacturing site wear gloves, overalls and full-face respirators. Given the engineering controls and supplementary personal protective clothing (PPE), the health risk for workers at the manufacturing site is expected to be low.

After synthesis, the notified polymer is transported to the moulding site. Exposure of transport and storage workers is only possible in the event of accidental spillage. The health risk for transport and storage workers handling the notified polymer is expected to be negligible.

There is one moulding site in Australia. The injection machines connect directly to the bulk containers of notified polymer via a permanent enclosed hose and all the injection machines are operated automatically. The most likely points at which exposure may occur are during connecting and disconnecting the hose and during clean-up of the machines, through incidental skin or eye contact. Inhalation exposure is unlikely. Following injection moulding, the notified polymer is trapped within a matrix and becomes unavailable for absorption.

Local exhaust ports are fitted over the injection area and workers will wear gloves, protective clothing and safety goggles. The health risk for workers in the moulding site is considered to be low.

The MDI content of the 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 MDI below the 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 (ACGIH, 2000). The risk of occupational asthma from repetitive exposure to isocyanates is well known. Therefore, respiratory protection to prevent occupational exposure is indicated. The use of self-contained breathing apparatus should be considered to prevent worker exposure where the workplace risk assessment indicates that worker exposure may exceed the NOHSC exposure standard. Because of the sensitising properties of isocyanates, precautions to prevent exposure must be taken by all personnel, especially those who either have had prior contact with isocyanates or suffer from any form of compromised respiratory function (NOHSC, 1990). Health surveillance for isocyanates should be conducted (NOHSC, 1994a).

Public Health

Public exposure to the notified polymer in its liquid state is not expected, except in the event of an accidental spill. There may be extensive public contact with moulded shoe soles, however the notified polymer is bound within the matrix, and the exposure is limited. Consequently the health risk to the public from exposure to the notified polymer through all phases of its life cycle, is considered to be low.

13. RECOMMENDATIONS

To minimise occupational exposure to "Polymer in Witcothane EAP 2000D" the following guidelines and precautions should be observed:

- Employers should ensure that NOHSC exposure standard for MDI is not exceeded in the workplace;
- 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* (NOHSC, 1999b), workplace practices and control procedures consistent with State and Territory hazardous substances regulations must be in operation.

For products and formulations containing free MDI the following guidelines and precautions should be observed:

- Employers should ensure that NOHSC exposure standards for MDI are not exceeded in the workplace;

- Health surveillance should be conducted in the workplace in accordance with the NOHSC *National Model Regulations for Control of Workplace Hazardous Substances* (NOHSC, 1994a);
- Safety goggles, chemical resistant industrial clothing and footwear and rubber or neoprene gloves should be used during occupational use of products containing the notified polymer; where engineering controls and work practices do not reduce vapour and particulate exposure to safe levels, an air fed respirator should also be used;
- 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 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, 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 TLVs and BEIs.

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

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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.

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

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