File No: NA/525

August 1997

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Polymer in Melio Promul 51

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 Worksafe Australia which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment, Sport, and Territories and the assessment of public health is conducted by the Department of Health and Family Services.

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, Worksafe Australia, 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

For Enquiries please contact the Administration Coordinator at:

Street Address: 92 Parramatta Rd Camperdown, NSW 2050, AUSTRALIA
Postal Address: GPO Box 58, Sydney 2001, AUSTRALIA
Telephone: (61) (02) 9577-9466 FAX (61) (02) 9577-9465

Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

Polymer in Melio Promul 51

1. APPLICANT

Clariant Australia of 675 Warrigal Road CHADSTONE VIC 3148 has submitted a limited notification statement in support of their application for an assessment certificate for 'Polymer in Melio Promul 51'.

2. IDENTITY OF THE CHEMICAL

Polymer in Melio Promul 51 is not considered to be hazardous based on the nature of the polymer and the data provided. Therefore the chemical name, CAS number, molecular and structural formulae, spectral data and details of the polymer composition have been exempted from publication in the Full Public Report and the Summary Report.

Other Names:	Melio Promul 59 polyether polyurethane
Trade Name:	Melio Promul 51 (contains 21% notified polymer)
Number-Average Molecular Weight (NAMW):	2 000-4 000 (see comments below)
Maximum Percentage of Low Molecular Weight Species Molecular Weight < 1 000:	none (see comments below)
Polydispersity:	6.8-4.256
Method of Detection and Determination:	infrared analysis
Spectral Data:	an infrared spectrum was provided for the notified polymer; major characteristic peaks were found at: 1 100, 1 245, 1 365, 1 720, 2 830, 2 870 cm^{-1}

Comments on Chemical Identity

The notifier submitted two separate molecular weight determination reports, undertaken on separate test samples. The gel permeation chromatography (GPC)

analysis determined the NAMW to range between 2 630 and 2 640, while the size exclusion chromatography (SEC) analysis determined it to be 4 095. The notifier claims that as polymers, based on reactants and conditions, never build exactly the same molecules, discrepancies in the NAMW will always occur.

It is also claimed that the percentage of polymer below 1 000 as represented in both the GPC and SEC analyses, is more likely due to tailing; a peak indicating oligomers or monomers would be observable if there were a percentage less than 1 000. However, it is not necessarily believed that this is the case as the polymer has very large polydispersity values, which would indicate that the polymer has a wide range of molecular weights. A molecular weight distribution of this size can influence the properties of the polymer (1).

3. PHYSICAL AND CHEMICAL PROPERTIES

The physico-chemical data summarised below are for Melio Promul 51, which is an aqueous dispersion containing 21% of notified polymer.

Appearance at 20°C and 101.3 kPa:	milky white liquid
Boiling Point:	~100°C (as for water)
Specific Gravity:	1.01
Vapour Pressure:	2.3 kPa at 25°C (as for water)
Water Solubility:	not determined
Partition Co-efficient (n-octanol/water):	not determined
Hydrolysis as a Function of pH:	not determined
Adsorption/Desorption:	not determined
Dissociation Constant:	not determined
Flash Point:	not determined
Flammability Limits:	not determined
Autoignition Temperature:	not determined
Explosive Properties:	not determined
Reactivity/Stability:	the polymer is expected to be stable and not decompose under normal storage and handling conditions

Comments on Physico-Chemical Properties

The notified polymer is prepared as an aqueous dispersion in water and the notifier claims that it is miscible with water. It is believed that the polymer would form an emulsion with water, however it is agreed that the polymer would not display true water solubility as it contains mostly hydrophobic groups except for a low percentage of carboxylate salt.

The notifier does not expect the polymer to hydrolyse as they claim it does not contain any hydrolysable groups. The presence of several carbamate and urea functionalities are noted, however, which are known to hydrolyse. However, hydrolysis in the environmental pH range would be precluded due to the polymer's insolubility in water.

Due to the complex nature of the polymer the partition coefficient, adsorption/desorption and dissociation constant are difficult to measure. The notifier claims that the polymer is likely to have a very low partition coefficient. However, this would suggest high water solubility, and the polymer is expected to be only miscible in water. Therefore, it is expected that the partition coefficient would be high. Adsorptivity has a strong inverse correlation with solubility. Therefore, the low solubility of polyurethanes suggests that they, and thus the notified polymer, will have high adsorptivity coefficients. The polymer contains a dissociable carboxylic acid salt group with the pK_a expected to be in the range 3 to 5.

4. PURITY OF THE CHEMICAL

Degree of Purity:	not determined; a purity analysis of the polymer was not undertaken; the notifier claims that it is a fully reacted product
Toxic or Hazardous Impurities:	not determined
Non-hazardous Impurities (> 1% by weight):	not determined
Maximum Content of Residual Monomers:	not determined
Additives/Adjuvants:	none

5. USE, VOLUME AND FORMULATION

The notified polymer will not be manufactured in Australia. It will be imported as a component of Melio Promul 51, which will contain the notified polymer at a concentration of 21%. This product will be used for finishing leather in tanneries, and will be applied by roller coating.

Approximately two tonnes of the notified polymer will be imported annually for each of the first five years.

6. OCCUPATIONAL EXPOSURE

The notified polymer will be imported in 100 kg plastic drums, and will be transported by road to the notifier's warehouse, where they will be stored until delivery to customers. Transport and storage workers are not expected to be exposed to the notified polymer under normal circumstances.

The notifier estimates that tannery workers may be exposed to the notified polymer for approximately one hour per day. Workers will dilute Melio Promul 51 with water, and the finishing coat is applied by gravure process (roller coating) to leather. After application to the leather substrate, the polymer film is dried by passing the finished leather through a heat tunnel. The main route of exposure is expected to be dermal, although accidental ocular contact may occur. Inhalation exposure to the notified polymer is unlikely, due to the expected low vapour pressure of the notified polymer.

Workers may also be dermally exposed to the notified polymer during cleaning processes and technicians may be exposed to the notified polymer for up to one hour per day when performing quality control work on leather finishing mixes.

There will be significant worker contact with finished leather, although the polymer will be bound to the leather by this stage, and will not be bioavailable.

7. PUBLIC EXPOSURE

The notified polymer will not be available to the general public. Once the new polymer is incorporated into finished leather, it becomes biologically unavailable as it is bound to the substrate. Leathers treated by Melio Promul 51 will be used for a number of automotive and clothing applications, with which the public will make contact. Due to the high molecular weight of the notified polymer, its low potential for absorption across biological membranes and its fixation to the substrate once applied to leathers, use of treated leathers by the public is not expected to cause any significant public exposure.

8. ENVIRONMENTAL EXPOSURE

Release

There should be no release to the environment during transport and storage except in a major accident.

The notifier states that environmental release to the atmosphere is unlikely to occur as the product is applied by roller coater at room temperature, and the polymer is non-volatile.

At the leather tanneries the polymer product is applied by roller coater (gravure process). The notifier estimates that approximately 2% of the polymer product will be lost through this process. Based on experience from previous assessments, it is accepted that the roller coating process results in very little to no losses. Generally, the only losses generated are through the cleaning of the application equipment. Waste water washings are collected and treated in the on-site effluent treatment plant before being discharges to sewer.

Minor spills and drips during the above operations will be absorbed with sawdust or sand. Large spills will be contained and should be diverted to the plant's waste water treatment plant for appropriate treatment.

Empty drums containing residues of the polymer product will be sent to landfill.

Fate

The fate of the bulk of the polymer will be tied to the fate of the finished leather. Leather that has been treated with the polymer is expected to be used in making leather products. Most of the treated leather will be landfilled, either as trimmings during the making of leather articles or when the goods are finally disposed of.

The waste solution from the cleaning of rotogravure machines is diverted to the leather company's waste water treatment plant. Details of this treatment process were not given. However, it is assumed that wastes will generally be flocculated and desludged before being discharged to the sewer. Draft ANZECC Guidelines (for Tanning and Related Industries) state that treatment of wastes to be disposed of to sewer should achieve the quality required by the treatment plant for trade wastes (2). Release of the polymer to the aquatic environment would therefore be negligible.

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data were provided by the notifier, which is acceptable for polymers with NAMW greater than 1 000, according to the Act.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were provided, which is acceptable for polymers of NAMW greater than 1 000 according to the Act. Such polymers are too large to cross biological membranes (3, 4, 5)

The notifier has provided the following results in the Material Safety Data Sheet (MSDS). Toxicity to water flea (*Daphnia sp.*), EC_{50} greater than 100 mg/L; toxicity to activated sludge, IC_{50} greater than 100 mg/L. Reports were not made available.

The EC_{50} and IC_{50} values indicate that the notified polymer product (Melio Promul 51) is practically non-toxic to water fleas and bacteria from a waste water treatment plant.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

Most of the polymer will be disposed of to landfill with the leather to which it is cured or bonded to. There should be no environmental hazard from such disposal.

As Melio Promul 51 contains 21% of the notified polymer, the total annual discharge of the polymer to the treatment plants of all 4 tanneries is estimated at 42 kg. The company estimates that each tannery will use about 200 kg of Melio Promul 51 per week, treating 3 500 hides. This should result in 300 000 L of waste water. Four kilograms of Melio Promul 51 (2%) will be lost in the process, equating to 0.84 kg of notified polymer. Therefore, the concentration of notified polymer in the effluent discharged to the on-site waste water treatment plant would be around 3 ppm.

The notifier expects this concentration to be reduced with further dilution in the on-site waste water treatment plant and when the effluent is discharged to sewer. The majority of polymer is expected to be trapped during the treatment processes and disposed of as landfill or by incineration. Therefore, there should be no significant hazard to the aquatic environment.

Small amounts of the polymer may arrive in landfill in an uncured/dried form, *eg* from waste during the after tanning process and that adsorbed to sludge in the waste water treatment plant. These will remain bound to soil due to the very low water solubility of the polymer. Incineration of such waste will destroy the polymer producing water and oxides of carbon and nitrogen.

Overall, the environmental hazard from the proposed import rates and use of the polymer is negligible.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The MSDS for the notified polymer states that the acute oral LD_{50} for Melio Promul 51 is greater than 2 000 mg/kg, and that the product is not a skin or eye irritant, or a skin sensitiser. Original reports for these studies were not sighted. The NAMW of the notified polymer is 2 000 to 4 000, and the notifier states that there is no polymer species with molecular weights less than 1 000, and no residual monomer content (see above section 'comments on polymer identity' for comments on these parameters). The notified polymer is imported as an aqueous dispersion, and this product is not a dangerous good.

There is expected to be negligible occupational health risk posed to transport and storage workers handling the imported product containing the notified polymer, based on the lack of exposure under normal conditions and the expected low toxicity of the notified polymer.

Tannery workers and technicians will be exposed to the notified polymer for approximately one hour per day, while carrying out leather finishing process, cleaning and quality control processes. The maximum polymer concentration that will be handled is 21%, and the polymer will be handled for relatively short periods.

These factors, combined with the expected low hazard, indicated that the risk for these workers is low.

The likelihood of public exposure to the notified polymer following an accident during transport of Melio Promul 51 is low. Under normal conditions of transport, handling and industrial use, the likelihood of public exposure to this material is also low. There may be widespread public contact with finished leather articles that are coated with the notified polymer. All leather used for upholstery, clothing and similar applications is 'finished' in some way by application of polymer films, and this product appears to be fairly typical of polyurethane coatings used in numerous other applications. It is essential in leathers of this type to have good adhesion of the film to the substrate; to conform to automotive and other standards, finished leather undergoes adhesion and abrasion testing. The polymer in Melio Promul 51 is chemically stable, is strongly bound to the substrate, and thus will not be released to the user. On this basis, the potential for public exposure to the notified polymer during use of articles incorporating this material is minimal.

13. RECOMMENDATIONS

To minimise occupational exposure to Polymer in Melio Promul 51 the following guidelines and precautions should be observed:

- It is good work practice to wear industrial clothing which conforms to the specifications detailed in Australian Standard (AS) 2919 (6) and occupational footwear which conforms to Australian and New Zealand Standard (AS/NZS) 2210 (7) to minimise exposure when handling any industrial chemical;

- Spillage of products containing the notified polymer should be avoided, spillages should be cleaned up promptly and put into containers for disposal;

- Good personal hygiene should be practised to minimise the potential for ingestion;

- A copy of the MSDS should be easily accessible to employees.

14. MATERIAL SAFETY DATA SHEET

The MSDS for a product containing the notified polymer was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (8).

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, secondary notification of the notified polymer shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

16. REFERENCES

1. Napper, D. 1993, 'Polymer Molecules', in *Surface Coatings Association of Australia, Surface Coatings - Volume 1: Raw Materials and Their Usage. Chapter 3*, The New South Wales University Press, NSW.

2. ANZECC & ARMCANZ 1995, *Draft Effluent Management Guidelines for Tannery and Related Industries - December 1995*, Commonwealth of Australia, Canberra.

3. Anliker, R., Moser, P. & Poppinger, D. 1988, 'Bioaccumulation of dyestuffs and organic pigments in fish. Relationships to hydrophobicity and steric factors', *Chemosphere*, vol. 17, no. 8, pp. 1631-1644.

4. Nabholz, J.V., Miller, P. & Zeeman, M. 1993, 'Environmental Risk Assessment of New Substances under the Toxic Substances Control Act Section Five', in *Environmental Toxicology and Risk Assessment, American Society for Testing and Materials*, ASTM STP 1179, Philadelphia, pp. 40-55.

5. Connell, D.W. 1989, 'General characteristics of organic compounds which exhibit bioaccumulation', in *Bioaccumulation of Xenobiotic Compounds*, CRC Press, Boca Raton.

6. Standards Australia 1987, *Australian Standard 2919-1987, Industrial Clothing*, Standards Association of Australia, Sydney.

7. Standards Australia/Standards New Zealand 1994, *Australian/New Zealand Standard 2210-1994, Occupational Protective Footwear*, Standards Association of Australia/Standards Association of New Zealand, Sydney/Wellington.

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