File No: PLC/159

August 2000

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME**

# FULL PUBLIC REPORT

## Polymer P-11

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 Family Services.

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Director
Chemicals Notification and Assessment

# FULL PUBLIC REPORT

## Polymer P-11

## 1. APPLICANT

Rohm and Haas Australia Pty Ltd of 969 Burke Road, Camberwell, Victoria, 3124 and Clariant Australia Pty Ltd of 675 Warrigal Road, Chadstone, Victoria 3148 (ACN 069 435 552) have submitted jointly a Polymer of Low Concern notification statement in support of their application for an assessment certificate for Polymer P-11.

## 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.

**Marketing Name:** Melio Add 131

**Characterisation as a Synthetic Polymer of Low Concern**

| | |
|---|---|
| **Number-Average Molecular Weight (NAMW):** | > 1000 |
| **Maximum Percentage of Low Molecular Weight Species** | |
| **Molecular Weight < 500:** | <1% |
| **Molecular Weight < 1 000:** | <1% |
| **Polymer Stability:** | Stable |
| **Reactivity:** | Not reactive |
| **Charge Density:** | Neither polycationic nor polyanionic. |
| **Method of Detection and Determination:** | The polymer was detected using infrared spectroscopy and characterised by gel permeation chromatography. |

The polymer meets the criteria for assessment as a synthetic polymer of low concern under Regulation 4A of the *Industrial Chemicals (Notification and Assessment) Act* (1989).

## 3. PHYSICAL AND CHEMICAL PROPERTIES

The polymer is never isolated as a defined entity and the data provided was for a < 25% aqueous solution of the polymer.

| | |
|---|---|
| **Appearance at 20°C and 101.3 kPa:** | Milky white liquid. |
| **Particle Size:** | Not determined. The polymer is imported as an aqueous emulsion. |
| **Boiling Point:** | 100°C. The boiling point is determined by the water solvent. |
| **Water Solubility:** | < 93 ppm. See comments below. |
| **Density:** | 1.0 – 1.2 kg/$m^3$ |
| **Vapour Pressure:** | 2.27kPa at 20°C |
| **Partition Co-efficient (n-octanol/water):** | Log $P_{ow}$ = 6.6 (calculated – see comments below). |
| **Hydrolysis as a Function of pH:** | Not determined. The polymer contains ester linkages that could be expected to undergo hydrolysis under extreme pH. However, due to the low water solubility, this is unlikely in the environmental pH range of between 4 and 9. |
| **Adsorption/Desorption:** | Log $K_{oc}$ = 5.0. See comments below. |
| **Dissociation Constant:** | No dissociation constant data were provided, as the polymer has no units likely to dissociate. |
| **Flash Point:** | Not determined. The polymer is an aqueous emulsion and non-flammable. |
| **Flammability Limits:** | Not determined. |
| **Autoignition Temperature:** | Not determined. The polymer is not expected to undergo autoignition. |
| **Explosive Properties:** | Non-explosive |
| **Reactivity/Stability:** | Stable. Thermal decomposition occurs at >177°C. |

**Comments on Physico-Chemical Properties**

The water solubility of the polymer solution was determined using a method derived from American Society for Testing of Materials (ASTM) and OECD methods based on the principle that above the solubility limit there is undissolved material present which can be quantified by turbidity measurement. A series of dilutions of the polymer solution in water was prepared and their turbidity measured. The water solubility was determined to be < 93ppm by extrapolating to zero turbidity. The water solubility of the repeating unit (single combination of the two monomers) within the polymer was also calculated to be 0.028 mg/L using ACD software. Actual solubility may be somewhat higher as the more polar monomer outweighs the other by about 19:1.

Partition coefficient and adsorption/desorption were determined using ACD software calculations of the repeating unit. Whilst for the reasons given above values may be overestimates, the polymer is expected to become associated with the organic component of soils and sediments. Based on polymer structure (non-polar tail, polar head), the polymer will have surface active properties.

## 4. PURITY OF THE CHEMICAL

| | |
|---|---|
| **Degree of Purity:** | >99% |
| **Hazardous Impurities:** | None |
| **Non-hazardous Impurities (> 1% by weight):** | None |
| **Maximum Content of Residual Monomers:** | All residual monomers are present at 0.08% or less. One monomer is irritating to eyes and skin and is a skin sensitiser. However, all are below cut-offs for classification of the polymer as a hazardous substance. |
| **Additives/Adjuvants:** | None |

## 5. USE, VOLUME AND FORMULATION

The notified polymer is part of an aqueous emulsion at < 25% and the emulsion will be imported as part of a leather finishing binder product Melio Add 131 at 30-60%. At two customer sites, the binder will be added to a formulation used to treat raw leather in preparation for furniture and automotive upholstery manufacture.

The notified polymer will be imported at the rate of up to 19 tonnes/year for the first 5 years.

## 6. OCCUPATIONAL EXPOSURE

**Import, Transport and Storage**

The notified polymer will be imported within a leather finishing binder in 1000L Schutz semi-bulk containers or 120L plastic drums and transported by road to storage or directly to 2 customer sites. Ten to twenty personnel working 2-3 hours/day for 10-15 days/year will be involved in these initial transport operations. Since the product containing the notified polymer will be supplied to customers in the original import containers, these waterside, transport and storage workers will be exposed to the notified polymer only in the event of accidental puncture of the containers.

**Leather Treatment**

At the customer facilities, leather treatment will be conducted for 8 hours/day for 200 days/year. Four to six mixing operators will pump the imported leather finishing binder containing the notified polymer at <20% from the import containers or drums into a 2 tonne open head stainless steel mixing vessel. Other chemicals and water will then be added to formulate the leather basecoat. These mixing operators may be exposed to the notified polymer for up to 30 minutes/day. The notified polymer is non-volatile and the mixing areas are fitted with local and general ventilation. Therefore, worker exposure is likely only via the skin and eyes. To prevent exposure, workers will be equipped with neoprene gloves, safety glasses and coveralls.

The basecoat containing < 2% notified polymer will be decanted manually into a reservoir and applied to unfinished leather in an automated enclosed spray booth. Two to four plant operators will be responsible for these operations and may be exposed to the notified polymer for up to 8 hours/day. Because of the manual handling of basecoat, workers may experience dermal exposure to the notified polymer. To prevent exposure, workers will be equipped with neoprene gloves, safety glasses and coveralls.

Following the automated spray procedure, 6-8 leather handlers will manually transfer the wet basecoated leather to ventilated drying ovens and then to finished stacks ready for transport to leather furniture and automotive upholstery manufacturers. Exposure to the notified polymer during these separate operations may be possible for up to 6 hours/day. The spray booths and drying ovens are fitted with local ventilation and so exposure to the notified polymer is only likely via the eyes and skin during the manual transfer of wet leather to the drying ovens. Exposure will be controlled by personal protective equipment consisting of neoprene gloves, safety glasses and coveralls.

Following the drying process, transport personnel and between 50 and 100 leather furniture upholsterers may be exposed potentially to the notified polymer for typically up to 6 hours/day. However, once the basecoat is dried and covered with additional topcoats, the notified polymer is expected to be immobilised and unavailable for absorption and so exposure of workers involved in these operations to the polymer is not envisaged.

## 7. PUBLIC EXPOSURE

It is expected that during transport, storage and commercial use, exposure of the general

public to the notified chemical will be low. Public contact with the notified polymer is expected to be limited as on most articles of household and automotive leather furniture, the notified polymer will reside beneath 1-3 polyurethane or polyacrylate topcoats.

## 8. ENVIRONMENTAL EXPOSURE

### Release

The notifiers state that no repackaging of the notified polymer will occur and it will be stored in bunded areas until transported to the customer sites in the original import containers. Therefore, no release to the environment would be expected until the binder product is used in the reformulation and application of the finished pigmented leather basecoat at the customer sites in Victoria and Western Australia.

The notifiers indicate that up to 5% (660 kg/annum in Victoria and 280 kg/annum in Western Australia) of the polymer could be lost during cleaning of the mixing and spray equipment. The application spray process will result in a loss of <20% due to overspray (2700 kg/annum in Victoria and 1100 kg/annum in Western Australia).

The notifier indicated that, based on past experience, around 25% of the polymer could be lost in the factories through all causes, and this would amount to a maximum of 4700 kg per annum in Australia (3300 kg/annum in Victoria and 1400 kg/annum in Western Australia). However, most of this would be collected with other aqueous waste and treated in a wastewater treatment plant prior to discharge into the metropolitan sewer system. The wastewater treatment plant at the leather treatment factory includes unit operations such as flocculation, dissolved air flotation, belt filtration of sludge and final pH adjustment. Based on previous submissions from the company, it could be estimated that > 90% of the wasted polymer (3000 kg/annum in Victoria and 1300 kg/annum in Western Australia) would be separated from the water into the sludge, and this would presumably be either incinerated or placed into a landfill by the licensed waste disposal contractor. Based on these estimates, it is expected that around 330 kg of polymer would be discharged to the Melbourne sewer and 140 kg to the Perth sewer each year.

Any residual polymer not assimilated into the solid sludge will be released with the aqueous effluent. It is expected that due to the hydrophobic nature of the polymer, any released into the sewer system would rapidly become associated with organic material and assimilated into sewer sediments and/or sewage treatment plant sludge. When applied to leather, the polymer basecoat is overcoated with 1-3 layers of polyurethane or polyacrylate and becomes incorporated into a highly crosslinked matrix which is expected to be very stable. Little release of the polymer as a consequence of abrasion or leaching is expected.

Residual material in the import containers (approximately 1% of the import volume) is washed out with water and used in blending subsequent batches of the finishing mix. The empty drums will then be reused or disposed of to landfill by a waste contractor.

### Fate

The majority of the notified polymer will become firmly fixed to the leather protein. The fate of the majority of the polymer will be the same as that of the leather articles into which the product is made. At the end of their serviceable life these articles would be disposed of to

landfill, or possibly be incinerated.

From the above information it can be seen that there are two waste streams that will take the polymer off-site:

- sludge from the on-site treatment plant which goes to landfill; and,
- supernatant from the on-site treatment plant that goes to sewer and then a municipal sewage treatment plant (STP).

Polymer disposed of to landfill is unlikely to be leached out because it has low solubility and is inert following treatment in the on-site treatment plant. The polymer is not expected to cross biological membranes, due to the low solubility and high molecular weight, and as such should not bioaccumulate (Connell, 1989).

## 9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data for the notified polymer were submitted. However, comments on the toxicity of polymers analogous to the notified polymer were submitted.

Lipacryl MB-2640 is an analogue polymer emulsion reported as non-irritant to eyes and slightly irritating to the skin with an $LD_{50}$ >5000mg/kg. E-1339 and E-1669 are also related aqueous polymer emulsions that show inconsequential to slight eye irritation and slight to moderate skin irritation with oral and dermal $LD_{50}$ >5000mg/kg. Acryloid 150, 154-70 and HF-833 are non-aqueous solution polymer products. Summarised toxicity data on these products containing polymer in dispersing oil show inconsequential to slight eye irritation and none to slight skin irritation. The $LD_{50}$ for each was >5000mg/kg.

These analogues show low oral and dermal toxicity and in general, slight oral and dermal irritation. Although the amounts of polymer in the emulsion were not provided, the physicochemical properties of the analogous polymers are reported to be similar to the notified polymer and so the toxicological profiles are expected also to be similar.

## 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were submitted.

## 11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The polymer is considered to be a low hazard in the environment when used in leather coating operations as indicated. Almost all (approximately 90%) of the polymer waste will be removed as solid waste from the on-site treatment plants and disposed of to landfill by licensed operators where it will be unlikely to leach.

Only a small amount (10%) of the polymer waste will enter the environment through the sewerage treatment plants since the polymer is intended to be used at only two sites in Australia. Effluent from the Victoria site will enter the Werribee Treatment Plant. This plant handles approximately 500 ML/day (182.5 GL/year) of effluent. Effluent from the Western

Australia site will enter one of the southern STPs in Perth where the influent would be approximately 35 ML/day. The following table contains calculated predicted environmental concentrations (PECs) for both sites:

**Estimated daily PEC values**

| | Concentration based on 300 days/annum processing |
|---|---|
| In Werribee plant (500 ML/day) | 2.27 ppb |
| In receiving water (1:10 dilution) | 0.27 ppb |
| In Perth STP (35 ML/day) | 0.87 ppb |
| In receiving water (1:5 dilution) | 0.17 ppb |

The expected PEC of <1 ppb for both the customer sites is expected to pose a low potential hazard to aquatic organisms. While no aquatic toxicity data are available, polymers of this type are not likely to be toxic. Nonionic polymers with MW >1000 are held to be of low environmental concern (Nabholz et al., 1993).

Discarded leather products are also likely to be incinerated or placed into landfill where the notified polymer would be considered stable. The Material Safety Data Sheet (MSDS) provided by Clariant Australia Pty Ltd includes adequate directions for spill clean-up and subsequent disposal of material.

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

### Hazard Assessment

No toxicological data have been provided so the notified polymer cannot be classified according to the NOHSC *Approved Criteria for Classifying Hazardous Substances* (National Occupational Health and Safety Commission, 1999a). However, the high molecular weight and low content of low molecular weight species indicate that the polymer would be poorly absorbed across biological membranes. Moreover, the low residual monomer content and lack of reactive functional groups indicate that the notified polymer would be of low toxicity.

Limited data submitted on toxicity of analogue polymers confirm the likelihood of low oral and dermal toxicity and also indicate slight skin and eye irritant properties for the notified polymer.

### Occupational Health and Safety

Workers involved in initial import, transport and storage will only be exposed to the notified polymer in the event of accidental puncture of the semi-bulk containers or plastic drums. Despite the probable variability in levels of personal protective equipment worn by these workers, the low probability of exposure combined with the low anticipated toxicity of the polymer renders the health risk for these workers low.

At the leather treatment facilities, the main route of exposure to the notified polymer is via spillage of imported leather binder (<20% polymer) and formulated basecoat (< 2% polymer) during mixing and also the manual handling of wet leather from the spray booths to the drying ovens. In these cases, exposure is most likely via the skin and eyes. The low anticipated toxicity of the notified polymer combined with personal protective equipment consisting of neoprene gloves, safety glasses and coveralls to be worn by plant operators and leather handlers represents a low health risk.

Following the leather coating process, transport personnel and leather furniture and automotive upholstery workers may be exposed to the notified polymer. However, after drying, the notified polymer is expected to be bound irreversibly to the leather protein and 1-3 layers of topcoat and not available for absorption. Therefore, the health risk for workers involved in end- use of leather coated with the notified polymer is expected to be low.

**Public Health**

During the leather preparation process, crosslinking of the basecoat containing the polymer and leather will result in a high molecular weight film adhering to the leather substrate rendering the notified polymer biologically unavailable. In addition, on most treated leather articles the notified polymer will reside beneath 1-3 polyurethane or polyacrylate topcoats, which will preclude public contact. Consequently, the potential for public exposure to the notified polymer throughout all phases of its life cycle is considered to be low.

Based on the above information it is considered that the notified polymer will not pose a significant risk to public health.

## 13. RECOMMENDATIONS

To minimise occupational exposure to Polymer P-11, the following guidelines and precautions should be observed:

- Safety glasses or goggles, chemical resistant industrial clothing and footwear and impermeable gloves should be used during occupational use of the products containing the notified polymer. Where engineering controls and work practices do not reduce vapour and particulate exposure to safe levels, a organic vapour respirator should also be used;

- Spillage of the notified chemical should be avoided. Spillages should be cleaned up promptly with absorbents which should then be 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.

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).

## 14. MATERIAL SAFETY DATA SHEET

The MSDS for the product containing the notified polymer was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (National Occupational Health and Safety Commission, 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 subsection 64(1) of the Act, secondary notification will be required if the polymer characteristics cease to satisfy the criteria under which it has been accepted as a Synthetic Polymer of Low Concern. 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

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