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January 1999

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

K-97-003 Resin in Hydrholac PD

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT**K-97-003 Resin in Hydrholac PD****1. APPLICANT**

Rohm and Haas Australia Pty Ltd of 969 Burke Road CAMBERWELL VIC 3124 and Bayer Australia Ltd of 633-647 Springvale Road MULGRAVE NORTH VIC 3170 have submitted a limited notification statement in support of their application for an assessment certificate for K-97-003 Resin in Hydrholac PD.

2. IDENTITY OF THE CHEMICAL

Claims were made and accepted for the identity of K-97-003 Resin in Hydrholac PD to be exempt from publication in the Full Public Report. The data items were:

chemical name;
structural formulae;
molecular weight;
spectral data;
manufacturing sites; and
weight percentage and ingredients.

Trade Name: Hydrholac PD (containing 28-32% K-97-003 Resin)

CAS Registry No.: not assigned

Molecular Formula: the resin is a complex polymer and the molecular formula is unspecified

**Maximum Percentage of Low Molecular Weight Species
Molecular Weight < 1 000:** 0.8 ± 0.8 % (see comments below)

Method of Detection and Determination: GPC, IR

Comments on Chemical Identity

The notified polymer is a complex copolymer of high molecular weight and polydispersity, containing a large number of different functionalities. The polymer backbone contains a mix of ester and urethane linkages, which are distributed randomly within the chain.

The notifier provided a GPC trace and a summary analytical report supporting the number-average and weight-average molecular weight data provided. However, the GPC data was not of sufficient resolution to determine the content of low molecular weight species. This was estimated by extracting the dried polymer with tetrahydrofuran (THF), and weighing the residual solid following evaporation of the THF. The mean of three readings was taken.

The notifier also supplied an infrared spectrum which serves to identify and characterise the major chemical functionalities within the molecules.

3. PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties were derived from the commercial product Hydrholac PD, which is a 30% aqueous dispersion of the notified polymer.

Appearance at 20°C and 101.3 kPa:	opaque liquid
Boiling Point:	100°C (water)
Specific Gravity:	1.04
Vapour Pressure:	approximately 2.4 kPa at 21°C (water)
Water Solubility:	not determined (see comments below)
Partition Co-efficient (n-octanol/water):	not determined (see comments below)
Hydrolysis as a Function of pH:	not determined (see comments below)
Adsorption/Desorption:	not determined (see comments below)
Dissociation Constant:	not determined (see comments below)
Flash Point:	the aqueous dispersion is not expected to be flammable
Flammability Limits:	not expected to be flammable

Autoignition Temperature: not expected to be flammable

Explosive Properties: expected to be stable

Reactivity/Stability: expected to be stable

Comments on Physico-Chemical Properties

No water solubility data was supplied with the notification, however, the lack of polar residues in the polymer indicates low water solubility. The material is supplied as a 30% dispersion in water, and this is probably stabilised by surfactants or other adjuvants.

The polymer contains ester, urethane and urea groups. These are susceptible to hydrolysis under extreme pH conditions, but are expected to be stable in the environmental pH region where $4 < \text{pH} < 9$. The anticipated low water solubility would also lower the potential for hydrolysis by preventing intimate contact between the susceptible groups and the aqueous environment.

The partition coefficient was not determined. The notifier indicated that the polymer is expected to be surface active which precludes easy measurement of this parameter. However, it is likely that any surface activity of the new polymer (noting no surface tension data was provided) is a consequence of the surfactant and/or other adjuvants added to enable dispersion of the polymer in water. Nevertheless, the polymer contains many aliphatic hydrocarbon groups and few polar groups, therefore, would be expected to partition into the oil phase. Similar reasoning indicates that the polymer would associate with natural organic matter, and consequently could be expected to bind to the organic component of soils and sediments.

No dissociation data was provided. However, the polymer contains terminal urea functionalities which will have a weak basic reaction with water. This is supported by the pH of 8-9 for the dispersion, provided in the submitted MSDS.

4. PURITY OF THE CHEMICAL

Degree of Purity: > 99% (see comments below)

Residual Monomers: No data on the level of residual monomers was submitted, but it was indicated that after removal of all water and other solvent components from the formulation, the remainder was > 99% pure. The assessment presumes that very little residual monomer is contained in the formulation, a presumption supported by the small quantity of low molecular weight species present.

**Toxic or Hazardous
Impurities:**

<i>Chemical name:</i>	N-methyl pyrrolidone (NMP)
<i>CAS No.:</i>	872-50-4
<i>Weight percentage:</i>	5.5
<i>Comments:</i>	N-methyl pyrrolidone is on the NOHSC <i>List of Designated Hazardous Substances</i> (National Occupational Health and Safety Commission, 1994a) as a skin and eye irritant with a concentration cut-off of 10%. The acute toxicity of NMP is low, however, it has shown adverse effects in animal reproductive studies.

Non-hazardous Impurities: not specified

Degradation Products: thermal decomposition will produce oxides of carbon and nitrogen; small quantities of hydrogen cyanide and isocyanate vapours may also be released.

Loss of Monomers, Additives: expected to be negligible

Comments on Purity

During the curing process when treating the leather, the polymer molecules will cross-link and bond to the leather substrate. Consequently loss of residual monomers or low molecular weight oligomers is expected to be negligible since these species would be effectively “trapped” within the polymer matrix.

5. USE, VOLUME AND FORMULATION

The notified polymer, K-97-003 Resin will be imported as a 28-32% aqueous dispersion in 100 kg plastic drums. The product will not be formulated or repackaged in Australia. It is estimated that 30 tonnes of the product Hydrholac PD (containing approximately 10 tonnes K-97-003 Resin) will be imported in the first year, and that this may increase to 50 tonnes (containing around 17 tonnes K-97-003 Resin) after 5 years.

Hydrholac PD will be used in a finishing agent for leather upholstery in motor vehicles. The finishing mix is prepared manually by mixing the required volumes of Hydrholac PD from the drums with other chemicals including solvents, flow modulators, binders and pigments in an open top blending tank. The finishing mix is then manually decanted to a reservoir from which it is dispensed as required, and applied containing 3% of the polymer to leather by spray or sealed rolling machine. Following application to leather hides, the polymer is cured by passing the hides through steam heated driers at 70°C for 8-10 hours where the polymer

becomes bound to the leather substrate. The finished leather contains 0.1-0.2% notified polymer.

6. OCCUPATIONAL EXPOSURE

Workers who will handle the notified polymer include transport and storage workers, and processing workers.

The vapour pressure of the notified polymer was not determined, however, it is expected to be very low due to its high molecular weight. Therefore, inhalation exposure to vapour of the notified chemical is considered to be unlikely. Inhalation exposure to aerosol containing the notified polymer may occur if mists are generated, e.g. during spray use. Skin contamination is the main route for occupational exposure.

Transport and storage

The drums containing the notified polymer will be unloaded from the ship to trucks for road transport to warehouse for storage in a bunded area then transported and stored at the customer site. The notifier estimated that there are 3-5 transport and storage workers involved in this operation for 2-3 hours per day, 200 days per year. These workers are unlikely to be exposed to the notified polymer unless the drums are breached.

Formulation

Only one company in Australia will use Hydrholac PD containing the notified polymer. At the customer's facility, the product, water and pigments will be manually combined in an open top mixer to produce a finishing mix. There will be 5 finishing mixers, working 8 hours per day and 200 days per year. Usage of the finishing mix containing 3% of the notified polymer will be approximately 40 kg per day. This would normally be made up on one shift but could be done by any of 2 or 3 different workers. Product will be manually stirred but may be dosed by pump rather than manually poured.

The finishing mixers may experience occupational exposure to the notified polymer as they may manually handle large volumes of undiluted product when adding it to the mixing vessel. Potential exposure will mainly be via dermal contact. The notifier indicated that the workers will be required to wear long sleeved overalls, chemical splash goggles, safety boots and neoprene or butyl rubber impervious gloves to prevent skin and eye contact.

Leather treatment

The finishing mix will be manually decanted into a reservoir and applied to the untreated leather via spray and/or sealed rolling machine to form one coat of a two-coat finish. The spray machine is an enclosed cabinet with exhaust extraction and a cascading water system to capture overspray. Exhaust air is further treated through another dissolved air flotation (DAF) system which consists of a series of water screens to remove impurities. Operators will manually load and unload leather from the spray and/or rolling machines. The material will then cure in a steam heated dryer at 70°C. The finishing process for one batch of leather (660-880 hides) takes approximately 8-10 hours.

There will be 2 spray and/or roller coating machine operators and 4 leather feeders and removers. They will work 8 hours per day and 200 days per year. Workers may experience occupational exposure to the notified polymer except when feeding in leather to the treating process. The spray/rolling operators and leather removers will handle the notified chemical in diluted form (3%) only. The spray/rolling operators may have both dermal and inhalational exposure to the notified polymer, if spray mist is generated. Workers handling the treated, cured and dried leather may contact the polymer, however because it is fixed it will not be separately available for contamination or absorption. The notifier indicated that the workers will be required to wear long sleeved overalls, chemical splash goggles, safety boots and neoprene or butyl rubber impervious gloves to prevent skin and eye contact.

Drum reconditioning

Open head drums are used for Hydrholac PD. After using the contents, approximately 1 kg of material would remain in each drum. The empty drums are stored on site until the drum reconditioners pick them up for reprocessing. The solid waste is scraped from the drum and disposed of to a licensed waste landfill site. On some occasions, liquid waste in the drum will be flushed with water to a waste water tank and sent to a licensed liquid waste processor.

Workers will clean the plastic drums for drum reconditioning. Splashes may occur during cleaning. The concentration of the notified polymer in the cleaning waste will be low and exposure could be predominantly via dermal and/or ocular contamination.

There will be 2-5 workers for drum reconditioning. The notifier indicated that the workers will be required to wear long sleeved overalls, chemical splash goggles, safety boots and neoprene or butyl rubber impervious gloves to prevent skin and eye contact.

7. PUBLIC EXPOSURE

The product containing the notified polymer will not be sold to the public. The potential for public exposure to the notified polymer during transport and coating operations or from disposal is assessed as negligible. Although the public will make contact with the notified polymer on the surface of automobile upholstery, exposure will be low because of low concentration (0.1-0.2%), high molecular weight (>1 000) and the cured state of the notified polymer in the treated leather, which would not be bioavailable.

8. ENVIRONMENTAL EXPOSURE

Release

It was indicated that in leather finishing performed for 8 hours a day, 200 days a year, up to 5% (2 500 kg per year) of the polymer could be lost during transfer operations to the application equipment and in cleaning this machinery. Further losses of up to 5% could arise through overspray during spray application, and from residual liquid left in the empty drums of Hydrholac PD. The notifier gave no indication of the expected degree of fixation of the

new polymer to the leather, but any of the polymer which does not become bound to the leather would also be discharged to, and treated with, the combined plant effluent.

The notifier indicated that, based on past experience, around 15% of the polymer could be lost in the factory through all causes, and this would amount to a maximum of 7 500 kg of Hydrholac PD per annum. 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. It was stated that > 90% of the wasted polymer (annually 6 750 kg) would be separated from the water into the sludge, and this would presumably be either incinerated or placed into a landfill. Based on these estimates, it is expected that around 750 kg of Hydrholac PD would be discharged to the sewer each year.

Any residual polymer not assimilated into the solid sludge will be released with the aqueous effluent. However, it is expected that any polymer released to the sewerage 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 becomes incorporated into a highly crosslinked matrix which could be expected to be very stable. Therefore, little release of the polymer as a consequence of abrasion or leaching is expected.

Residual material in the drums is either scraped out of the drums or washed out with water. The solid or liquid waste is then disposed of by a waste contractor.

Fate

The polymer is not expected to be mobile within landfill, and the high content of hydrophobic residues indicates that it would become strongly associated with the organic component of soils. No information on biodegradation was submitted, but it is expected that the polymer would be slowly degraded through the action of abiotic and bacteriological processes when placed into landfills in association with sediments and sludges. In an aerobic environment the polymer would degrade to water and oxides of carbon and nitrogen, while under anaerobic conditions methane, ammonia and nitrogen may also be produced. Incineration of sludges containing the polymer would result in its destruction, with production of water and oxides of carbon and nitrogen.

It is probable that obsolete car seats would be disposed of to landfill, or incinerated, where the fate of the polymer would be as described above.

9. EVALUATION OF TOXICOLOGICAL DATA

Toxicity data are not required for polymers of NAMW > 1 000, but should be provided if available.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Ecotoxicology data are not required for polymers of NAMW > 1 000, but should be provided if available.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The environmental hazard from the notified polymer is considered to be low when used as a finish for leather as indicated. It is estimated that 15% of the new polymer (ie around 7 500 kg per annum) may be lost as waste from the preparation of treatment solutions, incomplete fixation to the leather and other causes. Due to the low water solubility of the new polymer, most of this residue (> 90%) is expected to become assimilated into the waste sludge from the water treatment facility at the customer site, and subsequently incinerated or placed into landfill. It is estimated that around 750 kg of polymer could be released each year to sewer, and this would become associated with organic particulate matter, and would then become assimilated into sewage treatment plant sludge or into sewer sediments.

The notifier provided a calculation for the Predicted Environmental Concentration (PEC) of the polymer resulting from the effluent discharged to the sewer. Based on 750 kg discharged in factory effluent per year, and assuming the discharge occurs for 200 days per year (ie 3.25 kg per day) in a volume of 30 000 litres per day, the calculated concentration of new polymer in the plant effluent is 40 mg/L. It is assumed this is diluted by a factor of 1:125 in the metropolitan sewage treatment plant, and by a further factor of 1:10 when finally discharged to the receiving waters, to give a final PEC of 32 mg/L. However, this is probably an overestimate. It is calculated that in a city like Melbourne with a population of 3 million, the overall daily volume of sewage discharged is around 450 million litres. Consequently the PEC in the overall sewage discharge would be around 8 mg/L. Assuming a further dilution of 1:10 when discharged to the ocean, the final PEC is 0.8 mg/L.

The polymer is unlikely to be mobile in a landfill and would remain associated with the organic component of soils. Under these conditions it would be slowly degraded to gases such as carbon dioxide, nitrogen, nitrogen oxides and possibly methane and ammonia through the agency of abiotic and bacteriological processes. Incineration would destroy the polymer with production of water vapour and oxides of carbon and nitrogen.

Old leather upholstery would also be disposed of into landfills or incinerators where the fate of the notified polymer would be as described above.

In summary, the notified polymer is not likely to present a hazard to the environment when it is stored, transported and used in the typical manner.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

As the notified polymer has high purity, high molecular weight and low percentage of low molecular species, absorption across biological membranes would be restricted. On the information available, the notified chemical is unlikely to be a hazardous substance. The product Hydrholac PD contains a hazardous substance, N-methyl pyrrolidone which is a skin and eye irritant. According to the MSDS, the product can cause irritation of nose and throat, headache and nausea via inhalation, and slight eye and skin irritation via dermal contact. The MSDS warns that prolonged repeated exposure to the product may cause possible adverse reproductive effects, based on the solvent content. An in-house exposure limit for NMP of 25 ppm TWA is introduced by Rohm and Haas Company. If airborne concentrations in the workplace exceed the exposure limit, the MSDS outlines a respiratory protection program that must be followed. The basis for choosing this limit was not provided.

Transport and storage workers

Transport and storage workers are unlikely to be exposed with the notified polymer unless the drums containing the notified polymer are breached. The health risk is considered to be negligible.

Formulation

Finishing mixers will handle the undiluted product manually. A long-term moderate dermal exposure to the notified polymer is expected for these workers. However, the occupational health risk in dealing with the notified polymer is considered to be low based on its expected low toxicity. Engineering controls include local exhaust ventilation at the point of vapor emissions. In order to minimise the occupational exposure, workers should wear long sleeved overalls, chemical resistant apron or other impervious clothing, safety goggles, safety boots and neoprene or butyl rubber impervious gloves to prevent skin and eye contamination for NMP.

Leather treatment

No exposure to the notified polymer is expected when feeding in the leather for treatment. Spray/rolling operators and leather removers will manually handle the diluted form of the notified polymer when decanting it into the reservoir. This task is conducted daily. Exposure will mainly be via dermal contact. In addition, the spray/rolling operators may experience inhalational exposure if spray mists are generated in this process. The leather removers may contact the notified polymer, however, by this stage, the polymer is fixed to the treated leather and therefore not bioavailable. The risk of adverse health effects due to the notified polymer for spray/rolling operators and leather removers is considered to be lower than for the finishing mixers because the notified chemical is present in lower concentrations.

The overall risk of adverse health effects, namely skin and inhalation, may be increased if significant exposure to the spray occurs, as NMP, which is present in Hydrholac PD, is a known irritant. The same personal protective equipment should be used as that for the finishing mixers. However, no safety goggles are needed for leather removers.

Drum reconditioning

Drum cleaners will handle the notified polymer in a more diluted form. Their exposure will mainly be via dermal contact, and ocular exposure may occur due to splashes. The occupational health risk is considered to be low because of the expected low toxicity of the polymer and its low concentration in the washing waste. Personal protective equipment should include long sleeved overalls, safety goggles, safety boots and neoprene or butyl rubber impervious gloves to prevent skin and eye contamination.

In all operations above, the MSDS recommendations for exposure limits and respiratory protection for NMP should be observed.

Public health

The product containing the notified polymer will not be sold to the public. The notified polymer will enter the public domain as automobile upholstery treated with the product containing the notified polymer (final concentration in treated leather: 0.1-0.2%). Based on the use pattern of the notified polymer and its physicochemical properties, K-97-003 Resin is considered not to pose a significant hazard to public health.

13. 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* (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.

14. RECOMMENDATIONS

To minimise occupational exposure to K-97-003 Resin in Hydrholac PD the following guidelines and precautions should be observed:

- Σ Safety goggles should be selected and fitted in accordance with Australian Standard (AS) 1336 (Standards Australia, 1994) to comply with Australian/New Zealand Standard (AS/NZS) 1337 (Standards Australia/Standards New Zealand, 1992);
- Σ Industrial overalls or apron should conform to the specifications detailed in AS 2919 (Standards Australia, 1987) and AS 3765.1 (Standards Australia, 1990);
- Σ Neoprene or butyl rubber impermeable gloves should conform to AS/NZS 2161.2 (Standards Australia/Standards New Zealand, 1998);

- Σ All occupational footwear should conform to AS/NZS 2210 (Standards Australia/Standards New Zealand, 1994). Spillage of the notified chemical should be avoided.
- Σ Spillages should be cleaned up promptly with absorbents which should be put into containers for disposal;
- Σ Good personal hygiene should be practised to minimise the potential for ingestion;
- Σ A copy of the MSDS should be easily accessible to employees.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Act, secondary notification of the notified chemical 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

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

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

Standards Australia (1987) Australian Standard 2919-1987, Industrial Clothing. Sydney, Standards Association of Australia.

Standards Australia (1990) Australian Standard 3765.1-1990, Clothing for Protection against Hazardous Chemicals Part 1 Protection against General or Specific Chemicals. Sydney, Standards Association of Australia.

Standards Australia (1994) Australian Standard 1336-1994, Eye protection in the Industrial Environment. Sydney, Standards Association of Australia.

Standards Australia/Standards New Zealand (1992) Australian/New Zealand Standard 1337-1992, Eye Protectors for Industrial Applications. Sydney/Wellington, Standards Association of Australia/Standards Association of New Zealand.

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

Standards Australia/Standards New Zealand (1998) AS/NZS 2161.2:1998 Occupational protective gloves, Part 2: General requirements, Standards Australia/Standards New Zealand.