

File No: NA/573

February 1998

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

Polymer in Densodrin LD 6359

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT**Polymer in Densodrin LD 6359****1. APPLICANT**

BASF Australia Ltd of 500 Princess Highway NOBLE PARK VIC 3174 has submitted a limited notification statement in support of an application for an assessment certificate for a polymer in Densodrin LD 6359.

2. IDENTITY OF THE CHEMICAL

Trade Names: Densodrin LD 6359

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa:	Clear yellow-brown liquid as 40% solution in water
Melting Point:	< 5°C
Boiling Point:	approximately 100°C (as for water)
Specific Gravity/Density:	1.2 g.cm ⁻³ at 20°C
Vapour Pressure:	low (see notes below)
Water Solubility:	250 000 mg.L ⁻¹ at 25°C (see notes below)
Partition Co-efficient (n-octanol/water):	not determined (see notes below)
Hydrolysis as a Function of pH:	none expected (see notes below)
Adsorption/Desorption:	not determined (see notes below)
Dissociation Constant:	not determined (see notes below)
Flash Point:	not determined below 100°C
Flammability Limits:	not determined

Autoignition Temperature:	not determined below 200°C (product containing the notified polymer)
Explosive Properties:	not explosive
Reactivity/Stability:	stable at ambient temperatures and atmospheric pressure

Comments on Physico-Chemical Properties

The data above are pertinent to the commercial product Densodrin LD 6359 which is a 40% solution of the notified polymer in water.

The Material Safety Data Sheet (MSDS) supplied with the notification indicates no data to be available on this property, but it is expected that the vapour pressure of a relatively high molecular weight polymer will be very low. Since the polymer is marketed and used in a 40% aqueous solution (as Densodrin LD 6359), the vapour pressure of this could be expected to be similar to that of water, ie around 18 mm Hg at 20°C.

The polymer is highly water soluble or at least dispersible in water, with formation of a homogeneous mixture containing at least 40% of the notified polymer by weight. However, given that the chemical composition of the new polymer is mainly hydrocarbon (hence hydrophobic) with only a small content of carboxylate groups which will have an affinity for water, the very high “solubility” of the new polymer is surprising. It is probable that the material is not soluble in the conventional understanding of the term, but a concentrated colloidal dispersion in water, somewhat similar to a concentrated emulsion. The high specific gravity of this solution (1.2 g.cm⁻³) reflects the high polymer content of this mixture.

Hydrolysis of the polymer has not been determined, but the material contains no chemical groups which would be susceptible to hydrolytic attack under usual environmental conditions.

The n-octanol/water partition function has not been determined, but the new polymer contains a high content of large hydrophobic alkyl chains (ie C₁₆H₃₃ -) which would have high affinity for the oil phase. However, the presence of the water soluble carboxylate groups would also confer some affinity for water, and consequently the new polymer is possibly surface active and demonstrate surfactant properties in dilute solution. The structural portion of the molecule containing the two carboxylate groups [ie the CH(CO₂)-CH(CO₂) groups] would also lend the polymer chelating properties for divalent cations such as Ca²⁺ and Mg²⁺ etc.

Adsorption/desorption has not been determined, but the high percentage of (hydrophobic) hydrocarbon content in the polymer indicates that it would have

strong affinity for organic material and would consequently be expected to bind with and become associated with the organic component of soils and sediments. The charge neutralisation implied by the chelation of natural divalent cations such as Ca^{2+} as described above would assist this process through mitigating the affinity of the unassociated carboxylate groups for water. The notifier indicates that the calcium salt of the polymer is insoluble in water, and consequently this material could be expected to associate strongly with organic matter.

The dissociation constant was not reported in the notification dossier, but the pKa of the polymer is expected to be typical of organic carboxylate groups, and to lie between 4 and 5.

4. PURITY OF THE CHEMICAL

Degree of Purity: high

Toxic or Hazardous Impurities: none

Additives/Adjuvants:

<i>Chemical Name</i>	<i>CAS No.</i>	<i>% Weight</i>
Water	7732-18-5	60

Degradation Product: None expected under usual environmental conditions

Loss of Monomers, Additives, Impurities: No losses expected

5. USE, VOLUME AND FORMULATION

The notified polymer will be imported into Australia, as Densodrin LD 6359, at a concentration of 40% in aqueous solution. Densodrin LD 6359 is a tan-coloured liquid with a slight odour.

The notified polymer will be used as a waterproofing agent for leather products, such as shoes or leather pads. Import volumes will be between 4 and 40 tonnes per annum during the first five years.

6. OCCUPATIONAL EXPOSURE

Densodrin 6359, which contains the notified polymer, will be imported by sea in 120 L polyethylene drums as part of a mixed load of chemicals. It will be transported by road from the wharf to the notifier's warehouse where it will either be stored or transported directly to the customer. Upon arrival at the customer's

premises, the sealed drums will be unloaded and stored in the customers storage area.

In the production area, Densodrin LD 6359 is removed from the drums using automatic dosing equipment, transferred to a mixing vessel and diluted with water to a concentration of 8 to 10%. The automatic dosing equipment is a fully enclosed system with a maximum spillage of 10 g per tonne. The mixture is pumped into the tanning drums, and animal hides are added and mixed for 6 to 8 hours. During this time, the notified polymer is taken up and fixed to the hides. At the completion of the tanning process, the hides are removed and allowed to dry.

The estimated total number of workers that may come in contact with the notified polymer will be less than five personnel. One laboratory assistant, with an estimated period of contact of 13 to 14 hours per week, will be conducting trials with the notified polymer. In the production area, three operators will be handling the product for a maximum of 12 times per 24 hour duration and for 2 to 3 minutes each.

The notifier also noted that local exhaust ventilation is employed at all work areas where natural ventilation is considered inadequate.

7. PUBLIC EXPOSURE

Following import, the notified polymer will be available only to industrial processors and not to the general public.

In the event of an accident, the spill will be contained and the material will be pumped into containers or taken up with an absorbent and disposed of according to local regulations. End-products containing leather treated with the new polymer will mostly be landfilled, either as trimmings during the making of leather articles, or when the leather goods are disposed.

Once the polymer is incorporated into the finished leather, it becomes biologically unavailable as it is 'fixed' to the substrate. It is therefore expected that the use of treated leathers by the public will not cause any significant public exposure.

8. ENVIRONMENTAL EXPOSURE

Release

During the tanning process the new polymer solution is pumped from the imported 120 L drums using automatic metering pumps to mixing vessel where it is diluted with water. The diluted mixture is then pumped to tanning drums each with a capacity for up to 2 tonnes of animal hides and tanning mixture where it is anticipated that the notified polymer would constitute between 3.2 and 4% by weight of the total weight of each tanning batch. The tanning process is performed over a 6 to 8 hour period during which time the notified polymer is taken up and fixed to the leather. The fixation rate of the new polymer has not been determined,

but information provided by the company based on experience with polymers of apparently similar constitution (specifically other Densodrin polymers) indicates that the fixation rate of the new polymer is expected to be in the vicinity of 95%. This figure is derived from comparison of COD (chemical oxygen demand) data for the tanning solutions before and after the tanning operation. Assuming the 95% fixation rate indicated by the notifier, 5% of the new polymer or up to 2 000 kg per annum (based on annual usage of 100 tonnes of Densodrin LD 6359) would be discharged with tannery effluent, and this in turn is discharged into the metropolitan sewage system. The customer tannery operates on a 24 hour 7 day per week basis, and it is expected that the tanning operations will continue all year round. The total volume of tannery effluent discharged per year is 150 megalitres, and consequently the average concentration of the new chemical in the plant effluent is estimated as 14 mg.L⁻¹. However, the notifier indicates that the predicted environmental concentration in the effluent is only 1.4 mg.L⁻¹ which was based on an estimated loss of only 0.5% of the notified material in the plant effluent stream. The figure of 0.5% polymer in the effluent was derived from laboratory data, but since there was no offered rationale for acceptance of this laboratory scale result in preference to the plant scale result of 5.0%, the adoption of the higher figure is considered to be the most appropriate.

The notifier also indicates that the tanning effluent contains up to 500 mg.L⁻¹ of Ca²⁺ ions, and consequently the residual polymer in the effluent would be in the form of the insoluble calcium salt which (see notes on physico-chemical properties above) is insoluble, and would be expected to associate with organic material in the receiving sewage and to rapidly become incorporated into sludge and sediments.

Once having entered the sewage system, the effluent stream would be substantially diluted (a factor of 1:10 is appropriate) and consequently the initial predicted concentration in the sewer would be 1.4 mg.L⁻¹, but this is expected to quickly drop to substantially lower levels as a result of the adsorption mechanisms described above.

Since the new polymer is fully miscible with water, it is expected that the residuals remaining in the drums would be washed out and added to subsequent batches of the tanning mixture, and following this the empty drums would be suitable for appropriate reuse or proper disposal.

Fate

As discussed above it is anticipated that some 500 kg per annum of the new polymer will be discarded with spent tanning liquor into the sewage system. However, the expected affinity of the new polymer for organic matter (particularly in the presence of naturally occurring divalent cations (see notes on physico-chemical properties above) indicates that this would quickly become associated with organic material which is present at high levels in raw sewage, and would consequently become assimilated into sewer sediments or into the waste sludge produced by the sewage treatment plant. In the sewer sediments the material would be slowly degraded through biological action, while it is likely that sewage plant sludge would be disposed of into landfills.

The hydrocarbon “backbone” of the polymer would normally be very stable and would not undergo chemical degradation, although slow biodegradation would be expected in a landfill environment through the agency of bacteria present in these facilities. However, in a series of ecotoxicity tests on a polymer with some chemical and structural similarities (known as Sokalan CP 2, see below section on Environmental Effects) in it was found that almost 100% of this polymer adsorbed rapidly onto activated sludge, and also that in a 28 day biodegradation test under aerobic conditions (modified OECD Screening Test) that biodegradation was extremely slow. However, because of the significant differences in the structures of the Sokalan CP 2 and the notified polymer particularly, the absence of $C_{16}H_{33}$ groups and presence of $-OC_{H3}$ groups in the former, no conclusions on potential biodegradation rates of the notified polymer should be drawn.

Incineration would destroy the polymer with production of water vapour and oxides of carbon, while when discarded into landfill, either with old articles or as a component of sewage sludge, the polymer is unlikely to be mobile.

Since the notifier indicates that most of the imported polymer becomes “fixed” to the leather, the fate of the majority of the product will be the same as that of the leather articles, most of which are likely to be shoes. In all probability the old shoes and other leather articles would be discarded at the end of their serviceable lives and be either placed into landfill or incinerated.

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data were provided, which is acceptable for polymers with a number-average molecular weight (NAMW) greater than 1 000 according to the Act. The high molecular weight of the polymer precludes transmission across biological membranes. Although, one of the impurities is listed on the Designated Hazardous Substances (1), it is present in low levels that it is unlikely to be of significance.

The notifier’s MSDS states that toxicity data obtained from products of similar composition to Densodrin LD 6359, indicate that the notified polymer is of low oral toxicity to rats with an $LD_{50} > 2\,000\text{ mg.kg}^{-1}$, and is not irritant to the eye and skin of rabbits.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Although not required by the Act for polymers with NAMW greater than 1 000, the notifier provided some ecotoxicology data for a polymer which is apparently analogous to the notified material in some ways. This polymer analogue is known as Sokalan CP 2 or Sokalan PG 537 and is a polymer formed from 2,5-furandione and methoxyethylene, but no NAMW was stated for the material. However, this material would be similar to the notified polymer in respect that both polymers contain pendant carboxyl groups, and it is this structural feature which can bestow

toxicity to some aquatic species, particularly to green algae on anionic polymers (2).

The toxicity data derived for the analogue polymer are given in the table below. Tests were conducted for the acute toxicity to fish (*Leucisus idus*) and on the inhibiting effects of the polymer on bacterial growth (*Pseudomonas putida*). Tests data on inhibition of algal growth were not provided.

Ecotoxicity data for Polymer Sokalan CP 2

Test	Species	Results (Nominal)
Acute Toxicity to Fish [DIN 38 412 Part 11]	Ide <i>Leucisus idus</i> (golden)	LC 50 (96 h) = 5,300 mg.L ⁻¹ NOEL = 2,150 mg.L ⁻¹
Growth Inhibition for Bacteria [Warburg Test]	Bacteria <i>Pseudomonas putida</i>	EC 10 (17 h) = 1,920 mg.L ⁻¹

A report detailing the conduct of the fish test accompanied the submission. This test series was performed over a 96 hour period at 20 ± 0.2 °C in 10 L of water of hardness 2.5 x10⁻³ mol.L⁻¹ of Ca²⁺, and with dissolved oxygen levels between 7 and 9 mg.L⁻¹ and pH around 8.0. Tests were performed at four nominal concentrations of the test polymer, ie 1,000, 2,150, 4,640 and 10,000 mg.L⁻¹, with 10 fish used at each test concentration. No mortality of the fish was observed below an exposure concentration of 4,640 mg.L⁻¹ over the complete test period. However, after 24 hours exposure to 4,640 mg.L⁻¹ of the test polymer two fish had died, and this rose to three after 96 hours. At the exposure to nominally 10,000 mg.L⁻¹, eight fish were dead after 24 hours, and all ten had died after 48 hours.

No report on the bacterial test accompanied the notification.

These data indicates that the polymer Sokalan CP 2 is non-toxic to the aquatic species against which it was tested, but as remarked above this polymer is only analogous to the notified material in some chemical aspects, and consequently these data should be used as an indication of potential toxicity of the notified polymer only. However, in reference 2 it is noted that the toxicity of carboxylate containing anionic polymers to algae is often mitigated by the presence of high calcium levels which bind to the carboxylate groups.

Consequently, although no specific data on the ecotoxicity of the notified material is available, the available evidence suggests that the new polymer will not exhibit toxic effects if released to the aquatic environment, particularly if released into the sewer in the relatively low (ie 14 mg.L⁻¹) concentrations indicated above with the parallel discharge of relatively high concentrations of soluble calcium.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The environmental hazard from the notified polymer is considered to be low when it is imported, stored and used as a waterproofing agent for leather in the indicated manner.

Most of the material will be strongly adsorbed to shoe leather or other leather articles where it will remain until these articles are discarded to either landfill or incineration. Incineration would destroy the notified polymer with production of water vapour and gaseous carbon oxides, while in a landfill the polymer is unlikely to be mobile and leach away, and would be slowly degraded to methane, carbon dioxide and water through the agency of slow biological and abiotic processes operative within these facilities.

Some polymer will be released to the Sydney sewage system in the tannery plant effluent where the concentrations (in the plant effluent) may be significant, and possibly as high as 14 mg.L^{-1} . However, while the polymer may be potentially toxic to algae as a consequence of the constituent carboxylate groups, this is unlikely to present a problem in a sewer main. In any case the potential toxicity would be mitigated by dilution with the sewage, chelation of the contained carboxylate groups with calcium ions which are also discharged in the tannery effluent in appreciable concentration (up to 500 mg.L^{-1}), and through rapid adsorption of the polymer onto the organic matter (present at high levels in sewage) with which it has a high affinity. Similarly, if released to the general water compartment (other than a sewer) the new polymer is unlikely to exhibit toxicity to aquatic species, but is expected to rapidly become assimilated into soils and sediments through association with the naturally occurring organic component of these materials. Once adsorbed into sediments etc, the material would be slowly degraded through mechanisms analogous to those operating in a landfill.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The occupational health risk posed to waterside and transport workers is minimal, given the expected low exposure under normal working conditions.

There is a low occupational risk for workers who will be potentially exposed to the notified polymer due to the nature of the work done and the enclosed processes involved in handling the polymer. In the production area, local exhaust ventilation over the tanning drums and weighing stations are installed to prevent exposure to the notified polymer. The possibility of incidental contact with the notified polymer is likely to be minimised by the use of personal protective equipment and following good industrial hygiene practices.

There are no adverse effects expected from inhalation of the polymer due to its non-volatility. The notified polymer is in a form of an aqueous solution which is used at ambient temperatures and therefore expected to have a negligible volatility under ambient conditions. It has a high molecular weight and would be expected to be poorly absorbed across biological membranes.

While public exposure to the notified polymer is possible following accidental spillage during transport, under normal conditions of transport, handling and industrial use, the likelihood of public exposure is very low. There may be widespread public contact with finished leather articles that are treated with the notified polymer, however, the polymer is expected to be strongly fixed to the substrate, and thus not to be released to the user. On this basis, the potential for public exposure to the notified polymer during use of treated leathers is minimal.

Based on the nature of the chemical and the data provided, the notified polymer is not considered to be hazardous. The polymer in Densodrin LD 6359 would not be classified as hazardous according to NOHSC's Approved Criteria for Classifying Hazardous Substances (3).

12. RECOMMENDATIONS

To minimise occupational exposure to the Polymer in Densodrin LD 6359, the following guidelines and precautions should be observed:

- It is good work practice to wear industrial clothing which conform to the specifications detailed in Australian Standard (AS) 2919 (3) and occupational footwear which conforms to Australian and New Zealand Standard (AS/NZS) 2210 (4) to minimise exposure when handling any industrial chemical;
- 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 either through landfill or incineration;
- Good personal hygiene should be practised to minimise the potential for ingestion; and
- A copy of the MSDS should be easily accessible to employees.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the notified chemical was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (9).

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 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

1. National Occupational Health and Safety Commission 1994, *List of Designated Hazardous Substances [NOHSC:10005(1994)]*, Australian Government Publishing Service, Canberra.
2. Nabholz J.V., M.P., Zeeman M., 1993, 'Environmental Risk Assessment of New Chemicals Under the Toxic Substances Control Act (TSCA)', in *Environmental Toxicity and Risk Assessment*, American Society for Testing and Materials, ASTM STP 1179, Philadelphia, pp. 40-55.
3. Standards Australia 1987, *Australian Standard 2919-1987, Industrial Clothing*, Standards Association of Australia, Sydney.
4. 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.
5. Standards Australia 1994, *Australian Standard 1336-1994, Eye protection in the Industrial Environment*, Standards Association of Australia, Sydney.
6. 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, Sydney/Wellington.
7. Standards Australia 1978, *Australian Standard 2161-1978, Industrial Safety Gloves and Mittens (excluding electrical and medical gloves)*, Standards Association of Australia, Sydney.
8. Standards Australia/Standards New Zealand 1994, *Australian/New Zealand Standard 1716-1994, Respiratory Protective Devices*, Standards Association of Australia/Standards Association of New Zealand, Sydney/Wellington.
9. 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.