File No: NA/620

February 1999

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Laroflex MP 15

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Director Chemicals Notification and Assessment

NA620

FULL PUBLIC REPORT

Laroflex MP 15

1. APPLICANT

BASF Australia Ltd of 500 Princes Highway NOBLE PARK VIC 3174 and Courtaulds Australia Pty Ltd of 115 Hyde Road YERONGA QLD 4103 have submitted a limited notification statement in support of their application for an assessment certificate for Laroflex MP 15.

2. IDENTITY OF THE CHEMICAL

The following requests for exempt information were accepted: chemical name, CAS No., molecular and structural formulae, constituents and toxic or hazardous impurities.

Other Names: Laroflex LR 8829

Trade Name: Laroflex MP 15

Number-Average

Molecular Weight (NAMW): 9 040

Weight-Average

Molecular Weight: 28 500

Maximum Percentage of Low Molecular Weight Species

Molecular Weight < 500: 0.9%Molecular Weight < 1 000: 0.3%

Method of Detection

and Determination: gel permeation chromatography

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C

and 101.3 kPa: fine white powder with weak odour

Softening Point: 46-48°C

Specific Gravity: approximately 1.24 at 20°C

Bulk Density: approximately 370 kg/m³

Vapour Pressure: no data available - see notes below

Water Solubility: completely insoluble - see notes below

Partition Co-efficient

(n-octanol/water): no data available - see notes below

Hydrolysis as a Function

of pH: no data available - see notes below

Adsorption/Desorption: no data available - see notes below

Dissociation Constant: no data available - see notes below

Particle size: $size (\mu m)$ %

size (µm)	%	
 > 1 000	0.2%	
$630 - 1\ 000$	1.0%	
400 - 630	1.6%	
200 - 400	8.1%	
100 - 200	12.6%	
63 - 100	9.5%	
40 - 63	13.0%	
< 40	54.0%	

Flash Point: not determined

Flammability Limits: not determined but not expected to be flammable – see

notes below

Autoignition Temperature: not determined

Explosive Properties: not determined but not expected to be explosive

Reactivity/Stability: not expected to be reactive

Comments on Physico-Chemical Properties

No test reports on the determination of physico-chemical properties were included with the notification.

The polymer is a high molecular weight solid with a softening point around 47°C. The relatively high specific gravity for the polymer of 1.24 reflects the high chlorine content (approximately 40%). However, the bulk density of the material when shipped is only 370 kg/m³, indicating the particles of solid polymer are porous, and/or may be irregularly shaped. The polymer is expected to have very low vapour pressure, and the faint odour of the solid is presumably due to the small content of residual monomers and impurities.

The notifier indicated that the new polymer is insoluble in water and while no test report was provided, it is accepted that a high molecular weight polymer of this nature would have very low water solubility. This is supported by its proposed use as a binder in marine antifouling paints. The notifier provided a summary of results relating to the extraction of residual monomers and other impurities from the polymer by water, and while this study has no direct relevance to water solubility of the polymer, it supports the reported low levels of residual monomers and impurities indicated in section 2.

The polymer contains a small proportion of reactive epoxide groups which would react with water to produce diol functionalities, but significant hydrolysis of the C-Cl, ester or ether bonds within the polymer is unlikely in the environmental pH region where 4<pH<9. The low water solubility of the polymer would also mitigate any tendency for hydrolysis through exclusion of water from the vicinity of susceptible groups or functionalities.

No data on the oil/water partition coefficient or adsorption/desorption was included with the submission, but the polymer is essentially hydrophobic and would tend to associate with the organic component of soils and sediments.

The polymer contains no carboxylic acid groups or other functionalities likely to dissociate or become ionised, therefore dissociation constant data are not relevant.

Due to its high chlorine content, the polymer would not be expected to be flammable.

4. PURITY OF THE CHEMICAL

Degree of Purity: approximately 100%

Toxic or Hazardous

Impurities: < 55.5 ppm

Non-hazardous Impurities

(> 1% by weight): none

Maximum Content

of Residual Monomers: 55.5 ppm

Additives/Adjuvants: none

5. USE, VOLUME AND FORMULATION

The notified polymer is to be used as a binder in marine antifouling paints. It will be imported in 20 kg paper bags in powder form at a rate of 1-5 tonnes per year for the first five years.

6. OCCUPATIONAL EXPOSURE

The notified chemical is to be imported in "special" paper bags in a container of mixed chemical products. Exposure to waterside, transport and storage workers should only occur in the event of accidental spillage.

At Courtaulds Coatings Pty Ltd where the paint containing the notified polymer will be blended, approximately 30 batches per year will be manufactured. Paint will be blended in 1 000 L batches containing the polymer at 7-8%. Therefore, approximately 60 kg or three bags of the polymer are added per batch. The notified polymer is manually added to solvent in the mixing vessel, which is fitted with solvent vapour and dust extraction. The polymer is first blended in the solvent then colourant, pigment, extenders, biocides, solvents and other ingredients (see Material Safety Data Sheet (MSDS)) are added prior to blending of the final paint. After samples are removed for quality control testing, the product is filtered and filled into 10 L containers. The potential for exposure to the notified polymer would mainly be confined to addition of the powder to the blending vessel. A high proportion of the polymer powder is likely to be inspirable ($\sim 90\%$), with an unknown proportion likely to be respirable (see section 3). As it is likely that dust clouds produced during addition of the polymer to the mixing vessel may not be removed quickly by the exhaust ventilation, inhalation exposure will probably occur.

The total number of workers involved in paint blending is less than 15. Likely personnel to experience exposure to the notified polymer at the paint blending facility will be one raw material storeman for approximately 10 minutes per batch, one factory operator for approximately 1.5 hours per batch, one chemist for 15 minutes per batch, one filling line operator for one hour per batch and two warehouse operators for approximately 5 – 6 hours per year. The notifier states that workers handling the powder wear industrial clothing, safety goggles, protective gloves, safety boots and aprons. An air-purifying (dust) respirator is available if dust is released to the atmosphere. Personal protective equipment used by workers on paint filling lines and by maintenance workers involved in pot cleaning will most likely be industrial clothing, protective gloves, safety boots and eye protection where necessary.

End use of the paints containing the notified polymer involves spraying onto the bottoms of large vessels in a dry dock. The notifier states that solvent drying from the spray results in overspray being confined in the dock, mainly as dust on the floor. There is potential for dermal, inhalation and ocular exposure to the paint while spraying. Paint sprayers are expected to wear industrial clothing, protective gloves, safety boots, eye protection, chemical

goggles and masks or half-face respirators.

7. PUBLIC EXPOSURE

The notified polymer will not be sold to the public, but will enter the public domain as marine anti-fouling paints containing the polymer at 7 - 8%. Public contact will be limited to those who paint their own boats, however, contact would be brief and intermittent. Exposure under such occasions would be low because of the moderate concentration of the polymer in the paint. Moreover, once the paint is cured, exposure to the polymer would be negligible, as it will be in the form of an inert water-insoluble film.

8. ENVIRONMENTAL EXPOSURE

Release

Some release of the solid polymer during paint blending is possible, however total losses are expected to be small. Some airborne release of fine particles may occur during emptying of the bags into the blending tanks, but these tanks are fitted with vacuum extraction equipment and it is expected that most of the fine particles will be trapped on the filter media, and would be eventually placed into landfill. While not specified in the submission, empty bags of polymer would be either incinerated or be placed into landfill. Some polymer may remain in the bags after emptying, but given the indicated method of emptying these into the blending tanks this is expected to be small, and would not be expected to exceed 1% of import volume - ie a maximum of 50 kg per annum.

The notifier indicates that up to 3% of the polymer may be lost during cleaning of the batch tanks (ie approximately 20-25 litres of paint lost per batch), which amounts to a loss of approximately 2.4 kg of polymer. The washings from the batch tanks are pumped to a sludge pit, and when this is full the contents are pumped to 200 litre drums for disposal by contractors. It is presumed that the sludge would be incinerated, or be deposited into landfill. Assuming 30 batches of the antifouling paint are produced each year, estimated loss of polymer by this route is around 72 kg per year.

It was indicated in the submission that around 1% of the paint may remain with the empty 10 litre containers after application of the paint, and this would also be placed into landfill. This is expected to amount to an annual release of up to 50 kg of polymer.

Total annual release of the new polymer to landfill from the routes indicated above is expected to be a maximum of 250 kg.

Although small quantities of the paint may be applied by brush or roller, the new paint would normally be applied to the hulls of ships by spray techniques, and the notifier indicated that up to 30% of the paint (and hence of the polymer) could be lost as a result of overspray. Consequently a further annual loss of up to 1 500 kg is anticipated, and this would cure and *FULL PUBLIC REPORT*

solidify in the bottom of the dry docks or around the slip ways and be collected for disposal. Again disposal would be through collection of the dried paint material and deposition into landfill or possibly incineration.

Once applied to the hulls of ships, the polymer will be a component of a highly crosslinked mass of paint where it is expected to be very stable, and no significant release through leaching or other mechanisms is anticipated.

Fate

The polymer is quite stable and is not likely to be readily biodegradable, as could be expected from its intended use.

Most of the material will be incorporated into a paint matrix on the hulls of ships where it is expected to remain until removed through overall deterioration of the paint in the ocean, or deliberate stripping in ship repair facilities in preparation for recoating. Paint flakes removed as a consequence of deterioration would be deposited in the ocean sediments. Old paint is usually stripped from ship's hulls by sandblasting techniques where (in Australian shipyards), the paint residues are collected in special filtering equipment and would then be placed into landfill with spent blasting medium. Although not expected to be readily biodegradable, the material would be very slowly degraded through the biological and abiotic processes operative in these facilities. Here it is expected to produce water, methane and oxides of carbon, while the chlorine component would eventually be mineralised to inorganic chloride salts.

Incineration of polymer residues or paint containing the new polymer would produce water vapour, oxides of carbon. The chlorine component would be converted to gaseous hydrogen chloride, or possibly be converted to inorganic salts and become incorporated into solid ash residues.

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data were supplied.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicity data were supplied.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The new polymer poses little hazard to the environment when used as a binder in marine paint as indicated by the notifier.

It is estimated that up to 250 kg per annum of the polymer could be released as a consequence of paint manufacturing, and up to 1 500 kg more as a consequence of application of the paint. However, all polymer lost in this way will become incorporated into a cured paint matrix where it will be very immobile and losses through leaching or other mechanisms are expected to be very low. Most paint released as a result of manufacturing or application losses would be incinerated or be placed into landfill where its fate would be as described below.

In normal use as a component of marine paint some of the polymer will be sloughed off the hulls of ships as a consequence of general deterioration, and would become associated with marine sediments. However, it is likely that when stripped off ship's hulls during vessel maintenance, most of the old paint containing the new polymer will be placed into landfill with used abrasive. Here it is expected to be very slowly degraded through the biological and abiotic processes operative in these facilities and would be slowly mineralised to water, methane, oxides of carbon and inorganic chloride salts. Incineration of the new polymer or paint containing the polymer would result in the production of water vapour, oxides of carbon and possibly hydrogen chloride.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The notified polymer has a NAMW greater than 1 000 which is expected to preclude absorption across biological membranes and any potential systemic effects. The levels of low molecular weight species (NAMW less than 1 000, 0.9%) and residual monomers (less than 55.5 ppm in total) should not lead to a hazardous substances health effects classification for the polymer according to NOHSC *Approved Criteria for Classifying Hazardous Substances* (National Occupational Health and Safety Commission, 1994a).

The risk of adverse health effects to waterside, transport and storage workers, to workers involved in paint formulation and to workers using the paint containing the notified polymer is expected to be minimal on the basis of its likely low hazard.

Workers involved in importation, transport and storage should only be exposed in the event of accidental spillage.

During paint reformulation, exposure to dust while manually adding the paint to the mixing vessel is controlled by local exhaust ventilation. However, there may be some dust cloud formation if this operation is not carefully conducted. To minimise the risk of respiratory effects employees should ensure that the level of dust in the atmosphere is maintained below the NOHSC exposure standard for inspirable dusts (10 mg/mg³) (National Occupational Health and Safety Commission, 1995). Following addition of ingredients the mixing vessel, the likelihood of occupational exposure is expected to be minimal since the processes leading to drum filling should be automatic.

End use of the paint containing the notified polymer can, in principle, lead to significant exposure to the paint, although exposure to the polymer will still be low as it is contained in the paint at a low level of up to 8%.

Overall, the risk of adverse health effects to workers involved in paint blending or spraying is limited to respiratory effects from inhalation of polymer powder when added to the mixing vessel. In this case the risk of respiratory effects is low where effective exhaust ventilation is used. The risk of adverse health effects resulting from exposure to hazardous monomers is low. Data on extraction of vinyl chloride monomer provided by the notifier suggested that it could not be detected following slow mixing of an aqueous suspension of the polymer for 14 days.

According to the MSDS for a typical marine anti-fouling paint supplied by Courtaulds, the major hazards are skin and eye irritation, respiratory irritation and central nervous system effects from inhalation of vapours. Exposure standards for various components are listed on the MSDS as follows: copper oxide, 1 mg/m³; xylene, 80 ppm; inorganic pigments, 10 mg/m³; hydrocarbon resin, 15 mg/m³; methyl isoamyl ketone, 50 ppm, and diuron, 1 mg/m³. Although exposure at these levels is unlikely during paint manufacture, during end use, particularly in the confined spaces used for spraying in dry dock, these levels could be exceeded. The use of appropriate personal protective equipment (see below) is indicated. This applies to paint workers and members of the public. The NOHSC *List of Designated Hazardous Substances* (National Occupational Health and Safety Commission, 1994b) lists the concentrations cut-offs for xylene as 12.5% and copper oxide as 25%. Both these figures may be exceeded in the paint.

The risk of adverse health effects to the general public from exposure to the notified polymer is negligible given its likely low hazard, low concentration in paint, and infrequent use by boat owners. Once the paint is cured, public exposure to the polymer is negligible as is the risk of adverse health effects following exposure.

13. MATERIAL SAFETY DATA SHEET

The MSDS for the notified chemical and for the paint into which it is to be formulated were provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (National Occupational Health and Safety Commission, 1994c).

These MSDS were provided by the applicant as part of the notification statement. They are 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 the notified chemical the following guidelines and precautions should be observed:

- Spillage of the notified chemical should be avoided. Spillage 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.
- 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);
- Industrial clothing should conform to the specifications detailed in AS 2919 (Standards Australia, 1987);
- Impermeable gloves should conform to AS/NZS 2161.2 (Standards Australia
 - /Standards New Zealand, 1998);
- All occupational footwear should conform to AS/NZS 2210 (Standards Australia /Standards New Zealand, 1994c);
- Good general and local exhaust ventilation should be employed during paint formulation and, where possible, during spray painting;

Where exposure to paint aerosols will result in exposure standards for paint components being exceeded, a mask or half-face respirator conforming to AS/NZS 1715 and 1716 (Standards Australia/Standards New Zealand, 1994a; Standards Australia/Standards New Zealand, 1994b) should be employed.

Labelling of the end use paint will need to conform with the requirements of the NOHSC *National Code of Practice for the Labelling of Workplace Substances* (National Occupational Health and Safety Commission, 1994d) in relation to the levels of hazardous ingredients, for example, xylene and copper oxide in the paint product.

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) Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(1994)]. Australian Government Publishing Service, Canberra.

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

National Occupational Health and Safety Commission (1994c) 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 (1994d) National Code of Practice for the Labelling of Workplace Substances [NOHSC:2012(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: ed. Exposure Standards for Atmospheric Contaminants in the Occupational Environment: Guidance Note and National Exposure Standards. Australian Government Publishing Service, Canberra.

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

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

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.

Standards Australia/Standards New Zealand (1994a) Australian/New Zealand Standard 1715-1994, Selection, Use and Maintenance of Respiratory Protective Devices. Standards Association of Australia/Standards Association of New Zealand, Sydney/Wellington.

Standards Australia/Standards New Zealand (1994b) Australian/New Zealand Standard 1716-1994, Respiratory Protective Devices. Standards Association of Australia/Standards Association of New Zealand, Sydney/Wellington.

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

Standards Australia/Standards New Zealand (1998) Australian/New Zealand Standard 2161.2-1998, Occupational protective gloves, Part 2: General requirements. Standards Association of Australia, Sydney.