File No: NA/589

June 1998

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Lodyne 106A

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Director Chemicals Notification and Assessment

FULL PUBLIC REPORT

Lodyne 106A

1. APPLICANT

Ciba Speciality Chemicals of 235 Settlement Road THOMASTOWN VIC 3074 has submitted a limited notification statement in support of their application for an assessment certificate for Lodyne 106A.

2. IDENTITY OF THE CHEMICAL

Trade Name: Lodyne 106A (product containing 29.5 to 30 % of

notified chemical)

Method of Detection

and Determination: Infrared (IR) spectra were provided by the notifier

3. PHYSICAL AND CHEMICAL PROPERTIES

Unless stated otherwise, the characteristics given below refer to the product, (Lodyne S-152B) containing less than 10% of the notified chemical.

Appearance at 20°C

and 101.3 kPa: Light yellow liquid

Boiling Point: 83°C

Specific Gravity: 1.12

Vapour Pressure: Not determined (see comments below)

Water Solubility: 1 000 mg.L⁻¹ (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: Not applicable

Flammability Limits: Not determined; the notified chemical is not

expected to be flammable

Autoignition Temperature: Not determined

Explosive Properties: Non-explosive

Reactivity/Stability: Notified chemical is considered to be stable

Comments on Physico-Chemical Properties

As the notified chemical is an organic salt its vapour pressure is expected to be low.

The water solubility of the chemical has not been determined. However, in the ecotoxicity and biodegradation studies stock solutions of between 1 000 and 2 000 mg.L⁻¹ were prepared without any undissolved material being observed.

The hydrolytic behaviour of the chemical has not been investigated. The chemical contains no functional groups that are likely to be susceptible to hydrolysis within the environmental pH range (4 to 9).

The notifier indicates that as the chemical is surface active a reliable partition coefficient cannot be determined. Due to its high water solubility the chemical is likely to have a low octanol/water partition coefficient (Log P_{ow}) but this may be offset by its surface activity.

Due to the anticipated high water solubility and expected low Log P_{ow} , the chemical should not bind strongly to the organic matter in the soil and may be mobile, but this may be influenced by surface activity.

The notified chemical has a quaternary amine group but contains no functional groups that would gain or lose a proton.

5. USE, VOLUME AND FORMULATION

The notified chemical is intended to be used as a surface active agent in fire fighting foam. It will not be manufactured in Australia but will be imported as a component of Lodyne S-152B at a concentration of less than 10%. Import volumes in the first five years will be up to 500 kg per annum. The product containing the notified polymer is expected to be sold directly to customers for reformulation and to be used for emergency situations such as fire-fighting.

6. OCCUPATIONAL EXPOSURE

The notified chemical will be imported as a product and transported from the docks by road to the customer's warehouse where it will be stored. The notified chemical will be contained in sealed 200 L steel drums. Two to four transport and storage workers will be handling the containers for approximately 3 hours per day, 12 to 24 days per year. They are unlikely to be exposed to the notified chemical during normal working conditions, unless the containers were breached

During formulation of the end-use product, 3 to 6 material handlers, blenders and drum fillers, will be exposed to the notified chemical for approximately 3 hours per day, up to 50 days per year. Initially the steel drums containing the notified chemical will be connected to a 2 800 L blending tank by tubing and the contents pumped. Other components are added and mechanically mixed. The blending tanks are open but fully guarded. Therefore there is the potential for workers to be exposed to the notified chemical during transfer and when fitting and disconnecting the lines. If exposure occurred it would most likely be via the dermal route.

Quality control workers will sample the blended end-use products and there is the potential to be exposed to the notified polymer during this process. These workers are expected to be involved in the process for approximately one hour per day, 20 days per year. The dermal route is the most likely route of exposure.

Blended product which contains approximately 0.15% of the notified chemical is mechanically drummed off into 200 and 20 L steel drums before transport to user sites. There is the potential for occupational exposure during the transfer process or when disconnecting the lines.

Maintenance of pumps and tanks will be carried out for intermittent, short periods of time. During this phase there is the potential for dermal exposure to the notified chemical

At the sites of use, the reformulated product will be handled by fire fighters. The product will be further diluted (0.015 to 0.009% notified chemical) in stream use during fire fighting. A hose and a nozzle is connected to the steel drum containing the reformulated product and the water flow draws the product containing the notified polymer and forms a foam spray. Dermal contact is likely to be the main route of exposure. Contact with the end-use product may be prolonged depending on the end use circumstances.

7. PUBLIC EXPOSURE

There is negligible potential for public exposure to the notified chemical resulting from use as a surface active agent in fire fighting foam. In the event of a transport accident, the spill is to be contained. Residual liquids can be absorbed onto sand or other absorbent material and transferred into a closable container for disposal by landfill. Spills should be prevented from entering storm sewers and drains. Water should not be used as a clean-up medium as large volumes of foam develop and slippery conditions may result. Emptied containers may contain residual product and should not be re-used.

There will be no deliberate release unless the product is used for fire-fighting. The product will be further diluted within the foam.

Most if not all of the fire fighting liquids are contained at the fire site by absorbing onto sand or other absorbent material for disposal by landfill. Minimal public exposure may result after use of the notified polymer in a fire or accidental spillage. Adequate measures are described by the notifier in the Material Safety Data Sheet (MSDS) to minimise the risk of public exposure during disposal, or in the event of accidental spillage.

8. ENVIRONMENTAL EXPOSURE

Release

Reformulation of the notified chemical will occur at one site in Victoria. The notifier estimates that a maximum of 5% of the imported product will remain in the import drums (corresponding to 25 kg of the notified chemical per annum). This residue will be disposed of by a waste disposal contractor. Residues from the washing of formulation equipment will be disposed of in a similar manner.

The greatest potential for release of the chemical is through its use in fire fighting foams. Such fires would include those in flammable liquid stores or vehicle accidents involving flammable liquid tankers. In the former case, the notifier states that the flammable liquid storage areas where the foam containing the notified chemical will be used are required to have fire water containment such as bunding, sumps and onsite water treatment plants. At least in New South Wales, the fire water will only be released to the sewer with prior consent from the local water authority. If consent is not granted the waste is to be disposed of at a liquid waste facility.

Fate

The fate of the chemical in fighting "real" fires (such as a tanker accident) is problematic, as it will depend on the size of the fire and the amount of water and foam needed to control the fire. It is likely that it could enter local waterways via

storm water drains, road surfaces and overland flow unless bunding of the accident scene occurred.

High temperature incineration would destroy the compound with evolution of water and oxides of carbon, nitrogen and sulfur, together with release of low molecular weight fluorocarbon compounds, and possibly hydrogen fluoride.

The biodegradability of the notified polymer was investigated in accordance with OECD test guideline 301D (Closed Bottle Test). During the test, 11%, 66% and 90% biodegradation [Biological oxygen demand (BOD) expressed as a percentage of the chemical oxygen demand (COD)] was observed after 5, 15 and 28 days, respectively (1). The results indicate the substance is readily biodegradable under the conditions of the test. This suggests that the perfluorinated part of the molecule degrades rapidly. However, Remde and Debus (2) were not able to establish the fate of fluorinated moieties in the biodegradation of three different fluorinated surfactants investigated. They concluded that in all cases the formation of a highly fluorinated water insoluble fragment with unknown toxicity could not be ruled out (even when one was readily degraded), and it is likely that the fluorocarbon portion will be persistent.

The notified chemical consists of a mixture of congeners with varying length of perfluoroalkyl chains (C_{4-8}). The potential for bioaccumulation of these congeners has not been investigated. The molecular weight of the congeners and the high proportion of carbon-fluorine bonds is consistent with a high capacity for bioaccumulation. However, the high water solubility (and consequential likely low partition coefficient) and ionic nature of the chemical would indicate that the chemical is unlikely to bioaccumulate (3)

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Acute Toxicity

No toxicity data are required for chemicals which will be imported at volumes of less than 1 tonne per annum according to the Act. However, data on Lodyne 106A containing approximately 30% of the notified chemical, is summarised below was provided by the notifier.

Summary of the acute toxicity of Lodyne 106A

Test	Species	Outcome	Reference
acute oral toxicity	rat	LD ₅₀ =2 500 mg.kg ⁻¹	4
skin irritation	rabbit	Moderate to severe irritant	5
eye irritation	Rabbit	Moderate to severe irritant	6

9.1.1 Oral Toxicity (4)

Species/strain: rat/Wistar

Number/sex of animals: 5/sex/test

Dose levels: 2 100, 2 600, 3 300, 4 100 and 5 000 mg.kg⁻¹

Observation period: 14 days

Method of administration: Gavage

Clinical observations: Predeath signs included soiling of body

areas, wetness of the anogenital area, diarrhoea, brown staining of the anogenital area, lethargy, ptosis, piloerection, ataxia, dyspnea, prostration, emaciation; normal body weight increases were observed in

most survivors

Mortality: all animals died at dose levels of 5 000 and

4 100 mg.kg⁻¹; 2 male and 5 female rats died

at doses of 3 300 and 2 600 mg.kg⁻¹

respectively; 2 female rats died at the lowest

dose of 2 100 mg.kg⁻¹

Morphological findings: all dead animals exhibited hydronephrotic

kidneys, stomach distension with fluid and gas and scattered discolouration of the liver and lung; 4 surviving animals exhibited

hydronephrotic kidneys

Test method: similar to OECD guidelines (7)

LD₅₀: 2 500 mg.kg-1 with a 95% confidence limit of

2 100 to 3 000 mg.kg⁻¹

Result: the notified polymer was of low acute oral

toxicity in rats

9.1.2 Skin Irritation (5)

Species/strain: rabbit/New Zealand White

Number/sex of animals: 6 females

Observation period: 1,3 and 7 days

Method of administration: 0.5 ml of pure notified polymer applied to an

intact site on the back of each rabbit for 24 hours

Draize scores (8):

Time after	Animal #					
treatment (days)	1	2	3	4	5	6
Erythema						_
1	3	2	2	2	3	3
2	^a 2	2	1	2	4	2
7	2	4	1	4	4	4
Oedema						
1	2	2	2	3	2	2
2	2	2	0	1	2	1
7	0	2	0	1	2	0

^{*} see Attachment 1 for Draize scales

Test method: modified OECD guidelines (7)

Result: moderate to severe skin irritant

9.1.5 Eye Irritation (6)

Species/strain: rabbit/New Zealand White

Number/sex of animals: 1 male and 5 females

Observation period: 1, 2, 3, 7 and 14 day

Method of administration: 0.1 mL of the notified polymer into the

conjunctival sac of the left eye

Draize scores (8) of unirrigated eyes:

 -	•	-	4	
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Animal	1	1 day	/	2	day	/S	3	day	'S	7	day	'S	14	l day	/S
Cornea	oª	-	4 ^b	Oª	ć	a ^b	O ^a	a	l ^b	o ^a	ê	a ^b	O ^a	á	b
1	¹ 2	2	<u> </u>	2	2	2	2	1		0	C)	0	C)
2	0	C)	2	1	1	0	C)	0	C)	0	C)
3	2	2	<u> </u>	2	2	2	2	2	<u> </u>	3	2	2	3	1	
4	0	C)	0	()	0	C)	0	C)	0	C)
5	2	1		3	1	1	2	1		0	C)	0	C)
6	3	1		3	2	2	3	2	<u>-</u>	0	C)	0	C)
Iris															
1		1			1			1			0			0	
2		1		1		1		1		0					
3		1		1			1		1		0				
4		1		1		0		0			0				
5		1			1		0		0		0				
6		1			1			1			0			0	
Conjunctiv a	rc	Cd	d e	r c	C ^d	d e	rc	Ca	d e	rc	C ^d	ď	rc	Cd	ď
1	3	3	2	2	3	2	2	2	2	1	1	0	0	0	0
2	2	3	3	2	2	2	2	2	3	1	1	2	0	0	0
3	3	3	2	3	3	3	3	3	3	2	3	2	0	2	1
4	2	1	1	2	1	1	1	1	0	0	0	0	0	0	0
5	2	2	2	2	2	2	2	2	1	1	1	1	0	0	1
6	3	3	2	3	3	2	3	2	2	2	2	1	1	2	1

Test method: similar to OECD guidelines (7)

Result: moderate to severe eye irritant

9.2 **Overall Assessment of Toxicological Data**

The notified chemical was of low oral toxicity in rats (oral LD $_{50}$ = 2 500 mg.kg $^{-1}$ with a confidence limit of 2 100 to 3 000 mg.kg⁻¹ (combined sexes). The notified polymer was a moderate to severe skin and eye irritant in rabbits.

On the basis of the toxicity studies summarised above, the notified chemical would be classified as hazardous according to the Approved Criteria for Classifying Hazardous Substances (9) in relation to skin and eye irritation.

see Attachment 1 for Draize scales opacity barea credness chemosis ^e discharge

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Although ecotoxicity data are not required for chemicals imported in quantities less than 1 tonne, the following ecotoxicity studies have been supplied on Lodyne S-106A by the notifier. The tests were carried out according to OECD Test Methods.

Species	Test	Concentration s mg.L-1	Result (mg.L-1)	Reference
Fathead minnow (Pimephales promelas)	96 h acute	0, 50, 64, 80, 100, 125	LC ₅₀ = 72.0 (95% CL;65.9 - 78.7)	(10)
Water Flea (Daphnia magna)	48 h acute	10, 13, 16, 20; 25	EC ₅₀ = 15.6 (95% CL; 14.4- 16.9)	(11)
Sewage microorganis m	3 h respiration	1,10, 100, 1000	EC ₅₀ = 250 (95% CL;198- 316)	(12)

The ecotoxicity data for the notified chemical indicate that it is slightly toxic to fish, moderately toxic to daphnia and practically non-toxic to sewage microorganisms. No data have been provided for the toxicity of the notified polymer to algae. As polymers containing quaternary functionalities are known to be around 6 times more toxic to algae than to fish (13), this would be required should the import of the notified chemical exceed 1 tonne.

The notified chemical was soluble in water at all concentrations tested. No observations of sub-lethal effects were recorded during the ecotoxicity studies.

Additionally, the following ecotoxicity data appears on the Material Safety Data Sheet (MSDS) for the product, Lodyne S-152B. The reports for these data were not provided.

Species	Test	Result (mg.L ⁻¹)
Fat head minnow (Pimephales)	96 h acute	LC ₅₀ = 683
Water Flea (Daphnia magna)	48 h acute	EC ₅₀ = 105
Sewage microorganisms	3 h respiration	EC ₅₀ > 1000

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The chemical will be primarily used as a foaming agent to fight fires that have flammable liquids as a fuel source. The main environmental exposure of the chemical will occur when it is used in fire-fighting training or actual use conditions. In the former case, conditions will be controlled, with bunding and traps preventing the release of both chemical and fuel, to the environment. Actual use may occur in areas where bunding or traps are used to prevent the release of the flammable liquids to the environment, such as storage areas or refineries or in uncontrolled situations such as tankers carrying flammable liquids.

For a fire in a flammable liquid store, the water/foam is contained and may be released to the sewer if approval is granted from the local water authority. The concentration of the chemical leaving the foam-forming nozzle is less than 0.009% (9 ppm). The release of the water/foam mixture to a metropolitan sewer will lead to a concentration in receiving waters of less than 90 ppb (assuming and a $10\times$ dilution on entering the sewer with a further $10\times$ dilution in the sewage treatment plant and no adsorption or degradation of the chemical). Lower dilution factors are likely in country areas and a maximum concentration of 450 ppb in receiving waters is possible. Both these concentrations are two to three orders of magnitude below the lowest measured acute effect (*Daphnia magna* 48 h immobilisation EC_{50} = 15.6 mg.L⁻¹) and the estimated toxicity to algae (one sixth the 96 h *Pimephales promelas* LC_{50} i.e. 72/6 = 12 mg.L⁻¹). Hence, discharge of the notified chemical into metropolitan or country sewers is not likely to present a hazard to aquatic organisms.

Should the chemical be used in fire-fighting on tankers or trucks carrying flammable liquids, there is potential for the release of the chemical to the environment. The number of accidents in which petroleum fuels, such as petrol, were recorded as the primary ignition source was more than 1000 in 1994, according to figures from the NSW Fire Brigade.

A realistic, worst case situation would, be an accident involving a fuel tanker, with runoff from the accident entering a lentic (still) water body with significant wild-life. Figures provided by the ACT Fire Brigade indicate that about 4 000 L of water might be used to cool the tanker. Another 4 000 L together with the foam might be used to control any fire associated with the tanker, eg from spilt petrol and ignition of cabin material. If the fuel load catches alight, then when the fire can be approached, more than 12 000 L of water/foam mix would be needed to control the fire.

In the situation where the fluid load catches alight, the total amount of the chemical applied would be about 1.5 L (0.009% \times 16 \times 10 $^{\circ}$ L [(4 + 12) \times 10 3 L). The density of 1.12 g.mL-1, gives 1.6 kg of the notified chemical potentially requiring dispersal. Some of this will be combusted/pyrolysed in the fire leaving the fluorinated residues, although the amount lost is expected to be small. Any notified chemical left would be associated with run-off from the accident site. Run-off into a pond of about 1 ha surface area and an average depth of 15 cm (volume of about

 $1.5 \times_6 10^6$ L) would give a maximum concentration of 1.1 mg.L⁻¹ (1.6 × 10⁶ mg/1.5 × 10 L = 1.1 mg.L⁻¹).

The above worst case estimate is an order of magnitude below the lowest measured acute effect ($Daphnia\ magna\ 48\ h$ immobilisation EC_{50} = 15.6 mg.L⁻¹) and the estimated toxicity to algae (12 mg.L⁻¹). However, this estimate makes a number of assumptions.

One important assumption is that all of the chemical applied to the fire would be associated with run-off from the accident site. The run-off may not all flow into the lake, with some of the run-off adsorbed by road surfaces and soil surrounding the accident site. Where possible, standard operating procedures of Australian fire brigades should operate to minimise run-off by containment and removal. Also, some losses might be expected through adsorption to sediment and particulate matter because of its surface activity. On entering the surface waters, some of the chemical may partition to sediment, with biodegradation of at least the hydrocarbon portion of the molecule.

Another assumption is that there would be uniform and complete mixing of the chemical in the receiving surface water. This may not occur, and would lead to localised points (eg the entry point of the run-off) where the concentration of the chemical would be elevated. This could have localised impacts on invertebrate and algal species, but the effect on fish might be limited as they have the greater ability to avoid contaminated sites. Additionally, the situations in which release to surface waters might occur are likely to be rare. Several factors would have to be met for the chemical to have a major environmental impact. These are: 1) a major accident involving a flammable liquid tanker in which the load would catch alight, 2) the run-off from the fire-fighting escaping to a lentic surface water, and 3) the concentration of the chemical remaining near those affecting aquatic organisms for a few days. In the later case it should be noted that: (i) the chemical is a surfactant and as such is likely to readily disperse in the pond; and (ii) the chemical is present in the fire fighting foam at around toxic levels to invertebrate and probably algal species; any dilution, for example from water used to cool tanker or water in the pond would bring it below toxic levels. Hence, the potential environmental hazard from this use is expected to be low.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The notified chemical has a molecular weight range between 632 to 414. This is sufficiently high to substantially limit transmission across biological membranes. In addition the water solubility and expected low fat solubility and resultant low log partition coefficient indicate a reduced potential for bioaccumulation. The notified chemical has a low vapour pressure. The notified chemical will be imported at a concentration less than 10% in a liquid formulation.

The notified chemical has low oral toxicity when tested with rats. Studies on irritation potential indicate it is to be a moderate to severe skin and eye irritant.

These effects were above the level requiring a hazard classification according to the Worksafe Australia's *Approved Criteria for Classifying Hazardous Substances* (9).

The highest occupational exposure is excpected to occur during blending operations. Skin and eye exposure is possible during drum connecting and mixing; blending tanks are normally open but well guarded. The mode of use of the notified chemical indicates that a high health risk through occupational exposure to the chemical is unlikely in spite of a hazardous toxicological profile. The potential for skin and eye irritation is the most likely occupational health and safety concern. The use of suitable skin and eye protection during handling of the product containing the notified chemical and where there is splashing from the blending mixer, should reduce this.

Since quality control inspections, disconnecting lines during drum filling of blended products and maintenance of pumps and tanks are carried out for intermittent, short periods of time and product contains very small amount of the notified chemical following mixing (0.3 to 0.18%), workers will normally only be exposed to small amounts of the notified chemical.

Based on the above information it is considered that the notified chemical will not pose an undue risk to occupational health when used in the circumstances described by the notifier.

The notified chemical will be used as a surface acting agent in fire fighting foam to be used by fire-fighters. Minimal public exposure may result following contact with accidental spills or following use as a fire-fighting foam. The main route of exposure in these situations would be dermal, and possibly ocular and inhalation. The probability of public exposure is minimised by the recommended practices during storage and transportation.

13. RECOMMENDATIONS

To minimise occupational exposure to the notified chemical the following guidelines and precautions should be observed:

- Safety goggles should be selected and fitted in accordance with Australian Standards (AS) 1336 (14) to comply with Australian/New Zealand Standard (AS/NZS) 1337 (15);
- Industrial clothing should conform to the specifications detailed in AS 2919 (16);
- Impermeable gloves or mittens should conform to AS 2161 (17);
- All occupational footwear should conform to AS/ANZ 2210 (18);

- Spillage of the notified chemical should be avoided, spillages should be cleaned up promptly with absorbents and put into containers for disposal;
- 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 product containing the notified chemical was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (19)

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. Ecotoxicity results for algae plus full details of tests performed on Lodyne S-152B, would be required should the level of the imported chemical exceed one tonne.

16. REFERENCES

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