File No: NA/315

Date: 2 January 1996

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Zirconium salt DPP-RA

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Director
Chemicals Notification and Assessment
2 January 1996

FULL PUBLIC REPORT

Zirconium salt DPP-RA

1. APPLICANT

Ciba-Geigy (Australia) Ltd of 140 Bungaree Road, Pendle Hill, NSW 2145 has submitted a limited notification statement in support of their application for an assessment certificate for zirconium salt DPP-RA.

2. IDENTITY OF THE CHEMICAL

Zirconium salt DPP-RA is not considered to be hazardous based on the nature of the chemical and the data provided. Therefore the chemical name, CAS number, exact molecular weight, molecular and structural formulae, composition data (including spectra) and details of volume of import have been exempted from publication in the Full Public Report and the Summary Report.

Chemical name:	Zirconium salt DPP-RA
Trade name:	Component of Irgazin DPP Orange RA pigment*
Molecular weight:	<500

3. PHYSICAL AND CHEMICAL PROPERTIES

The following data refer to the notified chemical (zirconium salt DPP-RA) and not to the pigment product.

Appearance at 20°C and 101.3 kPa:	White powder
Odour:	None
Melting Point:	>700 °C. Sample did not melt but changed composition above this temperature.
Density:	2,930 kg/m^3
Vapour Pressure:	Not determined as substance is a solid with a high melting point
Water Solubility:	0.03 mg/L zirconium at 20°C (OECD TG 105).

	0.18 mg/L phosphorus at 20°C (OECD TG 105). <100 ppb (zirconium salt DPP-RA).
Fat Solubility:	Not determined
Partition Co-efficient (n-octanol/water) log P_{OW}:	Not performed due to low water solubility.
Hydrolysis as a function of pH:	Stable at 50°C for 5 days at pH 4, 7 and 9 (OECD TG 111).
Adsorption/Desorption:	Not performed due to low water solubility.
Dissociation Constant pKa**:**	12.1 at 20°C (calculated from solubility data).
Flash Point:	Not determined.
Flammability Limits:	Does not burn.
Combustion Products:	Not determined.
Decomposition Temperature:	>1500°C
Decomposition Products:	$(ZrO)_2P_2O_7$
Autoignition Temperature:	Does not burn.
Explosive Properties:	Not determined.
Reactivity/Stability:	Not expected to react exothermically with flammable material due to absence of reactive groups that could support oxidation. Does not react with moisture or moist air.
Particle size distribution:	*Notified chemical:* Mean diameter = 34.5µm. *Admixture with Irgazin DPP Orange RA:* Mean diameter = 0.33µm (99.9% < 2 µm)

Comments on physico-chemical data:

The company did not provide studies for partition coefficient and adsorption as the low water solubility of the notified chemical did not warrant the tests to be conducted. Also, the degree of adsorption of the notified chemical onto clay material would be less than the detection limit of the analytical instrumentation available (i.e., < 0.1 ppb zirconium).

The above comments provided by the notifier are adequate.

4. PURITY OF THE CHEMICAL

Degree of purity : > 95%
Weight percentage in imported product: 10%

Toxic or hazardous impurities: None known

5. INDUSTRIAL USE

The notified chemical in admixture (10%) with Irgazin DPP Orange RA pigment (90%) - referred to as the pigment product - will be used mainly in industrial (including automotive) paints and decorative paints (including architectural and house paint) with minor usage (< 5%) in speciality printing inks (including outdoor advertising, metal decoration, vinyl film, speciality packaging and security printing).

The expected volume (of the notified chemical) to be imported is less than 400 kg per annum for the next 5 years.

6. OCCUPATIONAL EXPOSURE

The notified chemical in admixture with Irgazin DPP Orange RA pigment is packaged in sealed 20 kg cardboard boxes (with antistatic polyethylene liner) and will be imported by air freight and distributed to paint and ink formulators (<10 establishments) by road throughout Australia.

Exposure during transportation and storage will occur only in the event of accidental spills or mishandling, but under normal conditions workers will not be exposed to any significant amounts of the notified chemical.

Typically, the sequence of events in the production of paints and inks is as follows. Pigment is delivered to the reformulator and quality checked, weighed and transferred to the mill area (by fork lift, trolley or by hand). Pigment is then added (in stages to ensure thorough mixing) to the pre-mix vessel containing other raw materials (e.g., resin solutions, solvents, oil). The mixing process usually takes around 45 minutes. The mixture is then dispersed on bead mills, attritors or ball mills and following a quality check (dispersion quality) it is pumped into mixing tanks for further blending (with additives, solvents and resin) to form finished product.

Manufacturing processes such as this would normally require less than 100 kg of pigment per batch and be performed every 2 to 4 months per establishment. The concentration of the notified chemical in finished products is typically <1%.

The main source of worker exposure to the notified chemical during reformulation is from weighing and batching operations, where exposure to pigment powder aerosols is possible. In addition, laboratory technicians may be exposed during quality control and in-process testing of pigment and pigment formulations. The total number of workers (plant operators and laboratory technicians) potentially exposed during reformulation is expected to be less than 50.

Occupational exposure (of painters, printers etc.,) to the notified chemical during application of finished products is also possible, but will be reduced due to the fact that the notified chemical will be encapsulated in the resin/polymer/varnish mix. Spray painting of new cars usually employs an automated (electrostatic) application process that minimises worker exposure, whereas car repair finishers are likely to be exposed to higher levels, as evidenced by higher paint wastage figures. Exposure to the notified chemical in decorative paints may also occur, although not via inhalation. An estimated 30 spray painters, numerous house painters (including ~ 1000 professional painters) and 10 printers may be exposed to the notified chemical during use of formulated products.

7. PUBLIC EXPOSURE

The public is unlikely to be exposed to the notified chemical during the importation and manufacturing of paints and inks.

Industrial paints generally contain less than 1% of the notified chemical. In the application of automotive paints, it is estimated that less than 15% of the applied paint is overspray. Such emissions (equivalent to a maximum of 0.005 kg of the notified chemical per vehicle) would be collected and disposed to landfill. Public exposure to the notified chemical in industrial paints is therefore expected to be negligible.

The public may be dermally exposed to the chemical during the application of decorative paints. The chemical is not volatile and inhalation exposure would therefore be negligible. The chemical will be firmly bound once the paint has dried, resulting in negligible exposure via painted surfaces. Public exposure to the chemical in cured inks would similarly be negligible.

8. ENVIRONMENTAL EXPOSURE

Release

The notified chemical is not expected to be released to the environment until it is disposed of as wastes from reformulation or from application processes. It should be

noted the notified chemical will only be released into the environment as a component of a pigment mixture.

Release to the environment may occur from spills during transport of formulated products containing the notified chemical, or in the disposal of material spilt at the workplace.

The main releases to the environment are likely to occur from the formulation of products containing the notified chemical and the application of the subsequent product(s).

The manufacturing processes for paints and printing inks are similar and involve the weighing/batching of the pigment and mixing it with some liquid media (e.g., resin solution). Release to the environment may occur during this process. It is estimated that negligible amounts (< 0.1 kg/year) will be released to the environment during the reformulation processes. Dust collectors/air filters will limit release into the air, while filtration/sedimentation will reduce the release into the waterways. The residues from these pollution traps are likely to be disposed to landfill.

Industrial paints generally contain less than 1% of the notified chemical. In the application of automotive paints at car manufacturers, an electrostatic multiple-gun spray painting process is used which results in minimal overspray. It is estimated that less than 15% of the applied spray paint would be 'lost' as overspray. Such emissions contain high percentage of solvents (~50%) and other volatile paint components, which are required to pass through scrubbers before release to the environment. It is estimated that less than 0.003 kg of the notified chemical per vehicle would be wasted and landfilled. In applications at car repair finishers, where generally only part of a vehicle is repainted, wastage may be as high as 50%. For this case less than ~0.005 kg of the chemical per vehicle would require disposal to landfill.

High quality surface coatings are formulated to be resistant against weathering (eg breakdown by light) and any release of the notified chemical by weathering of the paint film would be very gradual and diffuse. The amount of notified chemical per vehicle is estimated to be less than 0.02 kg. Any release by weathering is expected to be insignificant and diffuse.

Decorative paints are estimated to contain less than 0.1 - 0.2% of the notified chemical. As the coverage of decorative paints is typically 14 - 16 m^2/L, it is estimated that a painted article would contain less than 0.15 g/m^2 of the notified chemical. Applications are usually by brush or roller. The notified chemical is generally not emitted into air in these applications. Brushes and rollers are usually cleaned with a solvent or water and the washings disposed to sewers. It is estimated that 0.1 - 0.2 g of the notified chemical may enter the sewers per application. Any release of the chemical from the weathering of the painted article is expected to be insignificant and diffuse.

The notified chemical is likely to enter landfills as a result of the disposal of painted articles, empty paint cans and other solid waste.

Fate

The low volume of the chemical and its proposed use indicate its environmental fate is expected to be diffuse.

The low water solubility of the notified substance means that it should not easily move out of landfill areas after it has been deposited. Absence of adsorption/desorption makes analysis of the potential behaviour of the substance in waterways difficult, but given the low solubility of the substance, any free substance will most likely settle out onto sediments.

The notified chemical is a simple inorganic salt and is not expected to degrade. Also, the chemical is in admixture with a diketo-pyrrolo-pyrrole pigment which is not readily biodegradable (1).

Bioaccumulation of the notified chemical is unlikely to occur due to its expected low fat solubility and limited release to waterways.

9. EVALUATION OF TOXICOLOGICAL DATA

Under the *Industrial Chemicals (Notification and Assessment) Act, 1989,* as amended*,* toxicity data are not required for chemicals manufactured or imported in volumes less than 1 tonne/year. Also, the chemical is in admixture with a diketo-pyrrolo-pyrrole pigment which has been assessed (1) and found to be of low acute oral and repeat dose (28-day) toxicity (rat), neither irritating (rabbit) nor sensitising (guinea-pig) to skin and a mild eye irritant (rabbit). *In vitro* genotoxicity studies were negative. According to the available toxicological data, the pigment was not classified as a hazardous substance according to the NOHSC Approved Criteria for Classifying Hazardous Substances (2).

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Ecotoxicity studies were not provided and they are not required for limited notifications according to the Act. The notified chemical is in admixture with a pigment which would limit any potential environmental effects. Zirconium and its salts generally have low systemic toxicity (3).

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The low volume of the notified chemical and its proposed use throughout Australia indicates exposure to the environment will be diffuse and negligible. Therefore, the notified chemical is unlikely to present a hazard to the environment.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The notified chemical is likely to be of low oral and dermal toxicity in humans due to its expected low fat and water solubility (< 0.0002 g/L). Although the particle size of the notified chemical (~35µm) is outside of the respirable range, the mean particle size of the pigment admixture is 0.33µm (99.9% < 2µm), which is within the respirable range of < 7µm, and hence may cause lung irritation. The pigment admixture may also be slightly irritating to the eyes.

Aerosol generation is possible during reformulation processes, mainly during pre-mix operations (i.e., weighing, batching and transfer). After mixing, exposure (particularly via inhalation) to the notified chemical will be reduced due to its dilution and embedding in resin/solvent. Provided levels of airborne dust (for the notified chemical/pigment admixture) are kept below the Worksafe exposure standard for nuisance dusts (10 mg/m^3), exposure to the notified chemical should not exceed 5 mg/m^3 (TWA) - the Worksafe exposure standard for zirconium compounds (4). Ventilation controls used to reduce exposure to solvents during reformulation are expected to be adequate to control potential eye and lung irritation caused by the pigment admixture.

Dermal exposure to the notified chemical is possible before and after mixing, however, provided recommended precautions are taken to prevent skin and eye contact, topical effects (dermal/eye irritation) will be minimised. In addition, adverse systemic effects (from dermal absorption) are unlikely due to the expected low fat solubility of the notified chemical.

Workers using formulated products containing the notified chemical will be required to use appropriate engineering controls and personal protective equipment (ppe) to minimise exposure to solvents present in paints and inks. As the notified chemical will be present in very low concentrations in finished products (<1%), measures implemented to control solvent exposure should be sufficient to control any hazards due to the notified chemical.

Explosion/fire risks from static discharge during emptying of the pigment (containing the notified chemical) are minimised by antistatic plastic lined packaging, this permits safe discharge of contents in areas where solvent vapours are present.

In conclusion, when used under conditions which reduce dust generation to appropriate levels (Worksafe exposure standards) and provided appropriate safe work practices (including the use of ppe), the notified chemical presents a negligible health risk to workers.

The public may be dermally exposed to the chemical during the application of decorative paints, however at levels of 0.1-0.2%, it is unlikely to present a health hazard, particularly as the chemical will be firmly bound once the paint has dried.

13. RECOMMENDATIONS

To minimise occupational health and safety risks from zirconium salt DPP-RA the following guidelines and precautions should be observed:

- the filling date should be checked prior to discharge of pigment product from packaging. Should this date be more than 2 years old, the product should not be discharged in areas containing solvent vapours.

- atmospheric dust levels should be kept below 10 mg/m^3 (TWA) in accordance with Worksafe Exposure Standards for nuisance dusts (4).

- good industrial hygiene practices should be implemented during storage and handling.

- local exhaust ventilation should be implemented where there is a likelihood of aerosol generation.

- If engineering controls and work practices are insufficient to reduce exposure to the notified chemical, the following ppe should be used:

  respiratory protection should be chosen (to incorporate both a particulate filter and gas/vapour filter) according to Australian Standards AS/NZS 1715 (5) and AS 1716 (6);

  chemical-type goggles conforming to Australian Standards AS 1336 (7) and AS/NZS 1337 (8);

  impervious gloves conforming to Australian Standard AS 2161 (9); and

  protective clothing conforming to Australian Standard AS 2919 (10).

- a copy of the MSDS for the notified chemical admixture (i.e., Irgazin DPP Orange RA plus zirconium salt DPP-RA) and products containing this admixture should be easily accessible to all employees.

- appropriate safety phrases (i.e., S22 - avoid breathing dust and S51- use only in well ventilated area) should be included on label (for the notified chemical).

14. MATERIAL SAFETY DATA SHEET

The attached Material Safety Data Sheets (MSDS) for zirconium salt DPP-RA and Irgazin DPP Orange RA were provided by Ciba-Geigy (Australia) Ltd as part of their notification statement and are reproduced here as a matter of public record. Both MSDS were provided in Worksafe Australia format (11). The accuracy of this information remains the responsibility of Ciba-Geigy (Australia) Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989*, secondary notification of zirconium salt DPP-RA shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise.

In addition to these circumstances, secondary notification will be required if the notified chemical is either imported *per se* or manufactured in Australia.

16. REFERENCES

1. National Industrial Chemicals Notification and Assessment Scheme (NICNAS), Full Public Report, *Irgazin DPP Orange 16AOA*. NA/238 (21/2/1995), Worksafe Australia, Sydney.

2. National Occupational Health and Safety Commission 1994, *Approved Criteria for Classifying Hazardous Substances* [NOHSC:1008], Australian Government Publishing Service, Canberra.

3. Merck and Company Incorporated, *The Merck Index* 11th edn, Merck and Company, Rahway, USA. p1602, 1989.

4. National Occupational Health and Safety Commission 1995, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* [NOHSC:3008], Australian Government Publishing Service, Canberra.

5. Australian Standard/New Zealand Standard AS/NZS 1715-1994. *Selection, use and maintenance of respiratory protective devices,* Standards Australia, Sydney.

6. Australian Standard AS 1716-1994. *Respiratory protective devices,* Standards Australia, Sydney.

7. Australian/ New Zealand Standard AS/NZS 1336-1994. *Recommended Practices for Occupational Eye Protection*, Standards Australia, Sydney.

8. Australian Standard AS/NZS 1337-1992. *Eye Protectors for Industrial Applications*, Standards Australia, Sydney.

9. Australian Standard AS 2161-1978. *Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves),* Standards Australia, Sydney.

10. Australian Standard AS 2919-1987. *Industrial Clothing,* Standards Australia, Sydney.

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