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## NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

## FULL PUBLIC REPORT

## SORANE ISO S410, S553, S500

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Director

Chemicals Notification and Assessment

## FULL PUBLIC REPORT

## SORANE ISO S410, S553, S500

#### 1. APPLICANT

ICI Australia (Operations) Pty Ltd, 1 Nicholson Street, Melbourne VIC 3000.

## 2. <u>IDENTITY OF THE CHEMICAL</u>

Trade name(s): Sorane Iso S410; Sorane Iso S553;

Sorane Iso S500: for convenience throughout these reports 'Sorane

Iso S410' will be used.

Number-average molecular weight: >1000

Maximum percentage of low molecular weight species

(molecular weight < 1000): 0.5%

## 3. PHYSICAL AND CHEMICAL PROPERTIES

The notified polymer is never isolated from the reaction product of manufacture of which MDI comprises >50% by weight. The physical and chemical properties reported below are those of the mixture unless stated.

Appearance at 20°C the mixture is a

and 101.3 kPa: white paste

Odour: odourless

Melting Point: 21°C

Specific Gravity: 1.20 @ 40°C

Vapour Pressure:

no information is available for the

polymer.

Water Solubility:

cannot be measured due to the reaction of the product with water

to form insoluble polyureas.

Hydrolysis as a function of pH:

cannot be measured due to

reaction of the product with water

to form insoluble polyureas.

Partition Co-efficient (n-octanol/water)

cannot be measured due to reaction of the product with

water to give insoluble polyureas and with octanol to give insoluble

polyurethanes.

Adsorption/Desorption:

behave

mixture is considered likely to

like 4,4'-diphenylmethane

diisocyanate (MDI) in reacting with the water in soil to form insoluble  $% \left( \frac{1}{2}\right) =\frac{1}{2}\left( \frac{1}{2}\right)$ 

polyureas.

Dissociation Constant:

cannot be measured due to reaction

of the product with water to form

insoluble polyureas.

Flash Point:

205°C for product; not available for

polymer.

Combustion Products:

In fires will burn, emitting carbon

monoxide, carbon dioxide, nitric

oxide, nitrogen dioxide. At

temperatures above 600°C, hydrogen

cyanide is formed.

Explosive Properties: Will not detonate as a result of

heat, shock or friction.

Reactivity/Stability: the reaction product will react

with moisture forming insoluble polyureas and releasing carbon

dioxide gas. Reacts exothermically with materials containing active

hydrogen groups.

Particle size distribution: No information is available on the

polymer. Not applicable to the

mixture which is a paste.

## 4. PURITY OF THE CHEMICAL

Degree of purity: < 50%

Toxic or hazardous impurities: see "residual reactants" below.

Non-hazardous impurities: (> 1% by weight) none

Maximum content of residual monomers/reactants:

Chemical name: 1-1'-methylenebis (4-isocyanato

benzene)

Synonyms: 4,4'diphenylmethane diisocyanate,

MDI.

**CAS No.:** 101-68-8

Weight percentage: > 50

Toxic properties: Exposure standard for all

isocyanates;

TWA  $0.02 \text{mg/m}^3$ STEL  $0.07 \text{mg/M}^3$ 

isocyanates are noted as

sensitisers (1)

inhalation LC<sub>50</sub> rat: 178 mg/m<sup>3</sup>

Skin and eye irritant

Group 3 carcinogen IARC melting point; 37.2°C boiling point; 194-199°C@5mm, vapour pressure 0.001mm @40°C (2,3).

## 5. <u>INDUSTRIAL USE</u>

The notified chemical, in the reaction product as a mixture with MDI, is used in the production of polyurethane soles for footwear. Initially, the new polymer will be imported into Australia in quantities of 100-1000 tonnes/annum. Manufacture of similar quantities will take place at a later date.

#### 6. OCCUPATIONAL EXPOSURE

Sorane Iso S410 will be transported and stored in 25, 60 and 225 kg closed head steel drums. It is classified as a dangerous good under the Australian Code for the Transport of Dangerous Goods by Road and Rail.

Workers will be exposed to the notified chemical during laboratory development procedures, during use of the polymer in the footwear industry and during the projected later manufacture of the polymer in Australia.

Sorane Iso S410 manufacture involves charging melted MDI and polyol to an enclosed reactor and drumming the resultant mixture to appropriate containers. Spills of the polymer may occur during filling and the notifier recommends that they be contained by bunding. The polymer mixture is transported as a dangerous good to footwear sole manufacturers. When manufacture commences, three workers will be exposed for up to two hours per day, sixty days per year.

During laboratory development, to occur during manufacture and testing of the chemical, three workers are expected to be exposed for up to eight hours a day, 15 days/year. Work will be carried out in a fume cupboard.

Shoe sole manufacturing involves the reaction of Sorane Iso S410 with a formulated polyester polyol blend to form a polyurethane elastomer. Sorane Iso S410 is melted in a hot air oven at 40-

 $45^{\circ}$ C. The reactants are pumped into the injection moulding machine tanks, mixed together by a high speed screw and injected into a mould to produce completed footwear soles.

Footwear machine operators will charge the warm (melted) polymer by pump transfer into machine tanks, operate the moulding machine, clean the machine and decontaminate empty drums. It is expected that 22 workers will be exposed eight hours a day for up to 230 days per year. Exhaust fans connected to a stack will remove vapour, aerosols or degradation products.

Workers handling the notified chemical at any stage of its manufacture or use will wear protective clothing, impervious gloves and safety glasses. Local exhaust ventilation will be used to minimise vapours or aerosols.

## 7. PUBLIC EXPOSURE

Under normal conditions, the potential for public exposure to Sorane Iso S410 is low. There is complete reaction of the polymer mixture with another polyol to form a stable and inert shoe sole. Some degradation of the shoe sole may occur under the action of sunlight, but this is expected to be minimal during the life of the shoe.

Initially the polymers are to be imported at a rate of 100-1000 tonnes per annum in 25, 60 and 225 kg closed head steel drums. Approximately 40 kg of waste polymer will be generated yearly during polymer manufacture. This liquid waste will be disposed of by incineration. Shoe sole offcuts (approx 5 tonnes per annum) will be disposed of to landfill. Residual polymer from drum decontamination (1.4 tonnes per annum) will be converted into an insoluble polymer to be disposed of to landfill. Empty polymer drums are shredded and disposed as metal scrap.

#### 8. ENVIRONMENTAL EXPOSURE

#### . Release

The notified substance will be imported from Europe and later manufactured at Deer Park, Victoria, Australia in the range 100 - 1000 tonnes per annum.

The polymer mixture Sorane Iso S410 will be distributed to 6 customers (locations not disclosed) in Australia in 25, 60 and 225 kg closed head steel drums where it will be used solely for the manufacture of polyurethane footwear soling.

In the event of accidental spillage, the 4,4'-diphenylmethane diisocyanate (MDI) component of Sorane Iso S410 could cause an immediate terrestrial or aquatic environmental hazard. Contamination of drains or water ways should be avoided by containing and absorbing the polymer mixture with wet sand or soil. Given the reactivity of MDI in water, the likely environmental hazard will abate rapidly with the formation of water insoluble polyurea.

It is estimated that approximately 40 kg per annum of waste polymer mixture will be generated during manufacture of Sorane Iso S410 at ICI sites. This liquid waste polymer will be incinerated by ICI waste contractor, Harper Waste Disposal, Coburg, Victoria.

Waste generated from shoe soling manufacture will come from two sources:

- Approximately 1.4 tonnes of polymer residue from drums will be converted to water insoluble polyureas and polyurethanes by reaction with water and disposed of, by Harper Pty Ltd, to landfill.
- Approximately 5 tonnes per annum of off-cuts from trimming footwear soles, after their manufacture by injection moulding from the 6 manufacturing sites, will be disposed of to landfill. The water insoluble polyurethane waste is not expected to be mobile or undergo degradation in the environment.

Given the low vapor pressure of the notified substance, atmospheric contamination during manufacture of Sorane Iso S410 and its formulation into footwear soling is unlikely.

#### Fate

The notifier states that by nature of its application and the inert nature of the finished product, the polymer is required to be stable under a wide range of conditions.

The polymer will form oxides of carbon and nitrogen, hydrocarbon fragments and water vapour on combustion.

Sorane Iso S410 residues from containers will be converted to water insoluble polyureas and polyurethanes and, as such, are not expected to hydrolyse or biodegrade in landfill conditions.

## 9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data were supplied for the notified chemical. This is acceptable under the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act) for polymers of average number molecular weight > 1000.

Some toxicological information on diisocyanato diphenylmethanes (MDI) was provided (4). MDI in the liquid form irritates the eyes producing watering and discomfort. Skin contact with MDI may cause "slight to mild" irritation and temporary brown discolouration of the skin. In rare cases dermatitis may occur. MDI may cause skin sensitisation. MDI-based compositions have an acute oral LD50 >5000 mg/kg. MDI vapour, aerosol or dust can act as a primary respiratory irritant with acute bronchial irritation and dyspnoea in more severe cases. Sensitised individuals may experience wheezing, tightness of the chest and shortness of breath. A nocturnal cough may be a symptom of sensitisation. Symptoms of respiratory irritation and sensitisation may be delayed for some hours after exposure. A hyper-reactive response to minimal concentrations of MDI may develop in sensitised persons.

The LC50 (4hr) in the rat of a aerosol of polymeric MDI was 370 mg/m $^3$  (4). Rats exposed to an aerosol of polymeric MDI for two years had chronic pulmonary irritation at high concentration (4). Some tumours occurred at doses of 6 mg/m $^3$  but not at doses of 1 mg/m $^3$ . The report stated there were no pulmonary effects 0.2 mg/m $^3$ . No raw data from these studies was provided nor was the original study referenced. The significance of the observations cannot be determined but the report attributed the tumourigenic effect to a prolonged high exposure leading to chronic irritation and lung damage.

## 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were provided, which is acceptable for polymers of NAMW > 1000 according to the Act.

However, ecotoxicological results were provided for MDI, present in the reaction product with the notified substance, indicating low toxicity to the test species.

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EC_{50} (Daphnia) > 1000 mg.L<sup>-1</sup> (24h)
 LC_{50} (Zebra Fish) > 1000 mg.L<sup>-1</sup> (96h)
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#### 11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The polymer is unlikely to present a hazard to the environment during its manufacture and its formulation into polyurethane footwear soling.

The notified substance is not expected to exhibit toxic characteristics because large polymers of this nature are not readily absorbed by biota.

The notifier indicates that liquid wastes generated from the manufacture of the polymer mixture will be approximately 40 kg per annum, which will be incinerated by Harper Waste Disposal, Coburg Victoria.

Wastes generated from footwear sole manufacture (5 tonnes of shoe sole off-cuts and 1.4 tonnes of polymerised drum residues per annum) will be disposed of to landfill.

# 12. <u>ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS</u>

No toxicology data on the notified chemical are available. However, as a polymer with a number average molecular weight >1000, it is not expected to be absorbed across the skin or gastrointestinal tract. The notifier, based on experience with similar polymers, expects Sorane Iso S410 to be a skin and eye irritant, a skin sensitiser and a respiratory irritant and sensitiser. Sensitisation with similar polymers is said to be rare but it is not clear how much variation in free isocyanate levels exists.

The notified polymer is never separated from the end product of the reaction mixture. The product thus contains over 50% constituents which are known respiratory and skin sensitisers and respiratory, skin and eye irritants and would possess the properties of these constituents.

During use of the polymer in the footwear industry, the polymer will be melted at temperatures of  $40-45^{\circ}\text{C}$  before placing the mixture in a machine tanks mixing and inserting into a mould. Both the polymer and the other chemicals in the reaction mixture have low vapour pressures and this is not expected to present an inhalation hazard, although precautions should be undertaken to reduce exposure to an absolute minimum.

Eye contact or exposure via the skin may occur through direct contact or through any formation of a mist or aerosol during transfer of material. Precautions are required to minimise any such contact and will be particularly important in the event of spills and accidents.

Spills may occur during the filling of polymer into drums at the end of the future manufacturing process. Emergency services workers may be exposed to the notified chemical in the reaction mixture in the event of a transport or storage accident.

If moisture is present during storage, the polymer may react and form carbon dioxide gas, which may lead to overpressurisation and rupture of drums.

#### 13. RECOMMENDATIONS

To minimise occupational exposure to Sorane Iso S410 the following guidelines and precautions should be observed:

- . Work practices using Sorane Iso S410 should be designed to recognise the presence of free isocyanates, representing more than 50% of the commercial product.
- . Workplaces where Sorane Iso S410 is used or manufactured should employ local exhaust ventilation for any processes where exposure may occur.
- . Workplaces should be monitored and exposure standards (1) for isocyanates observed.

- Workers manufacturing or handling Sorane Iso S410 should wear protective clothing conforming to Australian Standard 3756.1-1990 (5), impervious gloves conforming to Australian Standard 2161-1978 (6) and safety glasses conforming to Australian Standard 1337-1984 (7). If respiratory exposure is possible, respiratory protection conforming to Australian Standard 1715-1991 (8) should be worn.
- . Transport and storage of Sorane Iso S410 should be in accordance with the Australian Dangerous Goods Code (9).
- isocyanate decontaminant (a mixture of water 90%, concentrated ammonia solution 8% and liquid detergent 2%) mixed with a nonflammable absorbent carrier such as sand or a proprietary absorbent to give a form which may easily be applied with a shovel) (4) or with wet sand or soil. Personnel cleaning up should wear protective clothing, safety glasses, impervious gloves and respiratory protection conforming to Australian Standards, as above, to prevent contact with the skin or eye or inhalation of vapour.

#### 14. MATERIAL SAFETY DATA SHEET

Attached to this Full Public Report is a Material Safety Data Sheet (MSDS) for Sorane Iso S410. This MSDS was provided by ICI Australia (Operations) Pty Ltd as part of their notification statement. It is reproduced here as a matter of public record. However the accuracy of this information remains the responsibility of ICI Australia (Operations) Pty Ltd.

#### 15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals* (Notification and Assessment) Act 1989 (the Act), secondary notification of Sorane Iso S410 shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

## 16. <u>REFERENCES</u>

- (1) Exposure Standards for Atmospheric Contaminants in the Occupational Environment. Guidance Note [NOHSC: 3008 (1991)]; National Exposure Standards [NOHSC: 1003 (1991)], 3rd Edition, October 1991.
- (2) Sax's Dangerous Properties of Industrial Materials Eighth Edition, Lewis R. Sr. Van Nostrand Reinhold Ney York 1992.
- (3) RTECS Registry of Toxic Effects Of Chemical Substances. National Institute of Occupational Safety and Health, US.
- (4) MDI-based Compositions: Hazards and Safe-Handling Procedures, ICI Polyurethanes, Aug 1990.
- (5) Australian Standard 3765.1-1990. Clothing for Protection against Hazardous Chemicals Part 1 Protection against General or Specific Chemicals Standards Association of Australia Publ, Sydney 1990.
- (6) Australian Standard 2161-1978. Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves), Standards Association of Australia Publ, Sydney 1978.
- (7) Australian Standard 1337-1984. Eye Protectors for Industrial Applications, Standards Association of Australia Publ, Sydney 1984.
- (8) Australian Standard 1715- 1991. Selection, use and maintenance of Respiratory Protective Devices, Standards Association of Australia Publ, Sydney 1991.
- (9) Australian Code for the Transport of Dangerous Goods by Road and Rail. Australian Dangerous Goods Code.Fifth Edition. Australian Government Publishing Service, Canberra. September 1992