File No: NA/100

Date: 19 Dec 1995

19 Dec 1995

#### NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

### FULL PUBLIC REPORT

# ACRYLONITRILE/STYRENE/ALPHAMETHYL STYRENE/ N-PHENYLMALEIMIDE POLYMER

This Assessment has been compiled in accordance with the provisions of the Industrial Chemicals (Notification and Assessment) Act 1989 and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by Worksafe Australia which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Arts, Sport, the Environment and Territories and the assessment of public health is conducted by the Department of Health, Housing and Community Services.

For the purposes of subsection 78(1) of the Act, copies of this full public report may be inspected by the public at the Library, Worksafe Australia, 92-94 Parramatta Road, Camperdown NSW 2050, between the hours of 10.00 a.m. and 12.00 noon and 2.00 p.m. and 4.00 p.m. each week day except on public holidays.

For Enquiries please contact Ms Karen Bell at:

Street Address: 92 Parramatta Rd Camperdown, NSW 2050, AUSTRALIA

Postal Address: GPO Box 58, Sydney 2001, AUSTRALIA

Telephone: (61) (02) 565-9466 FAX (61) (02) 565-9465

Director

Chemicals Notification and Assessment

# FULL PUBLIC REPORT

## ACRYLONITRILE/STYRENE/ALPHAMETHYL STYRENE/ N-PHENYLMALEIMIDE POLYMER

# 1. APPLICANT

GE Plastics Australia, 175 Hammond Road, Dandenong, Victoria, 3175

# 2. IDENTITY OF THE CHEMICAL

Chemical name: poly [(benzene, ethenyl-)-

(benzene, ethenylmethyl-)-(2propenenitrile)-(1H-pyrrole-2,5-

dione, 1-phenyl-)]

Chemical Abstracts Service

(CAS) Registry No.: 94858-30-7

Other name: acrylonitrile/ styrene/

alphamethylstyrene/ N-phenyl

maleimide polymer

Trade name: SR91B

**Molecular formula:**  $[(C_8H_8)_w - (C_9H_{10})_x - (C_3H_3N)_y - (C_{10}H_7O_2N)_z]_n$ 

Structural formula:

Number-average molecular weight: > 20,000

Maximum percentage of low molecular weight species

(molecular weight < 1000):</pre> < 0.5%

The number average molecular weight and the maximum amount of low molecular weight species were determined by gel permeation chromatography (GPC).

#### Method of detection and determination:

No specific method has been developed.

#### Spectral data:

IR Spectrum principal peak  $1780 \text{ cm}^{-1}$ 

#### 3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa: pearl white solid beads

Odour: 'mild' odour possibly due

to residual styrene monomer

T<sub>(a)</sub> 130-140°C Glass-transition Temperature:

not determined, estimated Specific Gravity/Density:

to be  $\sim 1000 \text{ kg/m}^3$ 

Vapour Pressure: vapour pressure of a

polymer of NAMW >20,000 is expected to be negligible

Water Solubility: SR91B is a slight

> modification of a polymer type which is sparingly soluble in water. Overall, the solubility of SR91B is negligible and is

estimated to be less than 1 ppm.

Partition Co-efficient not applicable to a high

molecular weight polymer (n-octanol/water) log P<sub>O/W</sub>:

Hydrolysis as a function of pH: the polymer is unlikely to

hydrolyse under

environmental conditions.

Adsorption/Desorption: not determined. Dissociation Constant does not dissociate.

Flash Point: approx 350°C (estimated).

Flammability Limits: not flammable.

Pyrolysis Products: if grossly overheated, the

polymer melt will pyrolyse. Compounds produced include aromatic and aliphatic hydrocarbons (including styrene), ammonia, hydrogen cyanide, acrylamide, carbon monoxide, carbon dioxide.

**Decomposition Temperature:** ~290 °C

**Decomposition Products:** (see pyrolysis products)

Autoignition Temperature: >500° C (estimated)

**Explosive Properties:** the polymer is not

explosive. However, if dusts form they may be

explosive.

Particle size distribution: the polymer beads are

approx 0.2-0.3 mm diameter.

Only 0.3-0.4% of the

particles are less than 75

μm.

# 4. PURITY OF THE CHEMICAL

Degree of purity: approx 98%

Toxic or hazardous impurities: (see residual monomers)

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

Maximum content of residual monomers:

. **Chemical name:** alphamethylstyrene

CAS No.: 98-83-9 Weight percentage: <1%

**Toxic properties:** boiling point 152.4°C

alphamethylstyrene is a mild eye

irritant and a moderate skin irritant in rabbits (1) . Sax (1) states that it is 'mildly toxic' by inhalation.

Exposure standard

TWA 242 mg/m $^3$  (50 ppm), STEL 483 mg/m $^3$  (100 ppm) (2)

acrylonitrile Chemical name: 2-propenenitrile Synonym:

107-13-1 CAS No.: <0.1% Weight percentage:

Toxic properties: boiling point 77.3°C

> LD<sub>50</sub> rat (oral) 78 mg/kg, (dermal) 148 mg/kg, absorbed after inhalation; acrylonitrile is an experimental tumourigen and teratogen; in humans it causes narcosis, cyanosis and diarrhoea (1). Human mutagenic data.

Exposure standard

 $TWA 4.3 \text{ mg/m}^3 (2ppm) (2)$ 

Chemical name: styrene

> Synonym: vinylbenzene

CAS No.: 100-42-5 Weight percentage: <0.5%

Toxic properties: boiling point 146°C

LD<sub>50</sub> rat (oral) 500 mg/kg, LC<sub>50</sub> rat (inhal) 24 g/m $^3$ /4hr; suspected human carcinogen,

experimental carcinogen, teratogen. Eye and skin irritant, narcosis in

humans (1).

Exposure standard

TWA 213 mg/m $^3$  (50 ppm) STEL 426 mg/m $^3$  (100 ppm) (2)

Chemical name: N-phenylmaleimide

CAS No.: 941-69-5

Weight percentage: <1%

Toxic properties:  $LD_{50}$  (oral) rat 188 mg/kg (1), skin

irritant.

Additive(s)/Adjuvant(s): none

#### 5. INDUSTRIAL USE

SR91B will be imported by sea, either as the base polymer or as formulated pellets, in quantities of > 100 tonnes/annum for the next four years. The pure polymer will be reformulated before sale to manufacturers for use as an engineering plastic for the manufacture of parts, structures, and components for

the automotive, communication and electrical/electronic appliance industries.

The notified chemical has been in use in Japan for six years. No adverse effects arising from its use have been reported.

#### 6. OCCUPATIONAL EXPOSURE

Exposure may occur during

- . transport from the dock to the reformulation site
- . reformulation
- transport of reformulated product to the manufacturing site
- . manufacture of articles
- . maintenance of equipment

Approximately 20 workers will be involved in transport from the dock to the reformulation site. The polymer or the formulated pellets will be transported in multilayered 25 kg bags. Pellets may also be transported in 500 kg plastic lined boxes or 18 tonne bulk containers. Exposure during this operation is expected to be minimal unless an accident and/or spill occurs.

The polymer will be reformulated with pigments, additives or other polymers. Articles will subsequently be formed by injection moulding, blow moulding or extrusion. Both processes will heat the polymer to melting. Workers involved in formulation or manufacture may be exposed during loading of polymer beads into hoppers, blending, compounding or extruding melt to give reformulated products, product testing, packaging finished products and cleaning equipment, including fume extraction vents and piping. Workers may be exposed for 8 hours/week, 48 weeks of the year.

Maintenance workers will clean blocked dust-extraction ducting, repair machinery hoppers and other equipment which may be covered with polymer dust and extrusion and other plant machinery used for manufacture of articles from pellets. Additionally, repair workers at both reformulation and manufacturing sites will repair vacuum fume-extraction pumps. Maintenance workers will be exposed for approximately 1 hr per week over a 48 week period per year.

# 7. PUBLIC EXPOSURE

The most likely mode of public exposure is through dermal contact with articles such as automotive components,

telecommunication equipment and electrical/electronic appliances which can contain up to 97.4% of the notified polymer. The other route of public exposure is through inhalation of processing vapours which escape control devices at the manufacturing

site. The vapours are known to contain acrylonitrile, butadiene, alpha-methyl styrene, toluene, ethyl benzene, isopropyl benzene, n-butyl benzene, sec-butyl benzene, phenol and acetophenone (these were determined in an analytical determination of the composition of the vapour levels in the hood extraction chamber during the manufacture of a product containing the notified polymer and other polymers) at very low concentrations of between 0.22-4.2 mg/m<sup>3</sup>.

Although the polymer is neither flammable nor corrosive, it will burn to produce toxic gases such as carbon monoxide, carbon dioxide, nitrogen oxides, hydrogen cyanide and aliphatic and aromatic hydrocarbons. Contaminated water from fire hoses (domestic or industrial fires) will be washed into the metropolitan sewerage system.

Disposal of the notified polymer in the form of spilt beads and pellets (approx. 18 tonnes per annum) is to be by landfill. Discontinued used products containing the notified polymer are also to be disposed by landfill. Disposal into municipal sewerage or incineration is not a favoured method.

Hazardous decomposition products include ammonia, acrylamide, alkyl and aromatic hydrocarbons, hydrogen cyanide and oxides of carbon. However, the rate of decomposition is expected to be low.

## 8. ENVIRONMENTAL EXPOSURE

#### . Release

SR91B will be brought to Melbourne by sea and transported by road to GE's plant in Dandenong, Victoria. Transport from Dandenong to manufacturing plants will also be by road. Since the substance is a solid and is considered inert and water insoluble, accidental spillage should be able to be contained with minimal environmental exposure.

Manufacturing of SR91B resin is to be undertaken outside Australia. However, it is proposed to blend SR91B resin with various compounds in Australia to produce pellets of different colours for sale to customers. Reformulation and repackaging will take place at the GE Plastics factory in Dandenong, Victoria. The pigmented pellets are produced by a process of mixing, blending, extrusion, pelletising, sieving and packaging. The pigmented pellets are despatched to customers in Victoria, NSW and SA.

The notifier has indicated that at GE's factory in Dandenong an estimated 2.6% non-recyclable waste will be generated by the reformulation process. The maximum total waste to be disposed of to landfill will be 26 tonnes per year. There are not expected to be any releases to the aquatic environment. Non-recyclable polymer waste in pellet or blob form from the GE Plastics site will most likely be disposed of, as landfill, by contractors to BFI Waste Disposal Systems at Lyndhurst, Victoria. Non-recyclable polymer waste in powder

form from GE Plastics site will most likely be disposed of, as landfill, by contractors to Harpers Pty Ltd at either Lyndhurst, Tullamarine or Narre Warren North, Victoria.

The notifier's customers are expected to use SR91B for injection moulding or blow moulding. The broad process involved is transfer of blend in pellet form to hoppers, heating of blend until it melts, injection of molten blend into mould, water cooling of moulded product and release of product from mould. Given the solid nature of the pellet, spills during transfer should be contained and cleared with minimal environmental exposure. Contamination of the cooling water is unlikely as such water does not come in contact with the moulded plastic but recirculates through the equipment to regulate the temperature. The notifier has indicated that scrap and rejected articles are usually recycled with virgin material. It is expected that less than 1% of the resin pellets will be non-recyclable and disposed of to landfill. The average expected waste volume disposed of to each customer's landfill site will be in the order of 1.25 tonnes per annum.

#### . Fate

The notifier states that by nature of its application and the durability required of the finished product, the polymer is required to be stable under a wide range of conditions. The polymer is not expected to hydrolyse in landfill conditions and due to its water insolubility is unlikely to enter groundwater.

#### 9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data are required under the <code>Industrial</code> <code>Chemicals</code> (<code>Notification</code> and <code>Assessment</code>) <code>Act</code> 1989 (the Act) for polymers of average number molecular weight > 1000. No testing has been carried out, although the acute oral toxicity of <code>SR91B</code> has been estimated overseas to be in excess of 5000 mg/kg.

The polymer, of molecular weight > 20,000, is not expected to be absorbed across biological membranes nor is it expected to have skin or eye irritant or sensitising properties specific to the polymer.

#### 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

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

#### 11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The polymer is unlikely to present a hazard to the environment when incorporated into pigmented injection moulding products.

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 wastes generated from resin powder reformulation to pigmented pellets will be no greater than 2.6% resulting in a maximum disposal volume to landfill of 26 tonnes per annum (total import volume of 1000 tonnes).

Non-recyclable waste from the notifier's customers is not expected to exceed 1% resulting in an average annual disposal volume to landfill of 1.25 tonnes. The customers are located throughout Australia resulting in a wide distribution of the substance, as plastic products and as non-recyclable waste disposed of to landfill.

# 12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The polymer itself has an average number molecular weight > 20,000 and is not expected to be absorbed across biological membranes. It is not expected to be a skin or respiratory irritant or a sensitiser. The polymer is presented in the form of beads of non-respirable size and the potential for dust formation is expected to be low but not entirely absent.

The boiling points of the residual monomers are below or close to the glass transition temperature of the polymer. Thus, the major hazard for workers with the polymer is exposure to vapours of residual monomers released on heating to form the polymer melt. These chemicals are all potential skin and eye irritants and are experimental or suspected human carcinogens. All are absorbed on inhalation. The vapours may cause narcosis, headache or nausea in humans. Precautions are required to prevent exposure.

Other vapours emitted in the use of the polymer may include trace amounts of acrolein, ethylbenzene, phenol, acetophenone, 4-vinylcyclohexene and cumene. All are skin, eye and respiratory irritants. Acrolein, ethylbenzene, phenol, cumene and 4-vinylcyclohexene are absorbed on skin contact or inhalation (1). Acrolein, ethylbenzene and phenol have produced tumours in experimental animals (1). N-phenyl maleimide may also be present in the processing vapour or condensate. Little toxicology data is available on this skin irritant. A analysis of extraction hood vapours during melt processing of SR91B with other polymers detected the monomers and other gases which may be emitted from the notified polymer: (exposure standard limits are included for comparative purposes)

	concentration in hood (mg/m <sup>3</sup> )	exposure standa TWA (mg/m <sup>3</sup> )	ard STEL
acrylonitrile	1.1	4.3	_
styrene	1.5	213	426
alphamethylstyrene	1.0	242	483
ethylbenzene	0.76	434	

phenol 4.2 19

acetophenone <1 ---
cumene 1 246

Such concentrations in an exhaust hood are not expected to lead to occupational hazards in a well ventilated workplace in the absence of malfunction.

Although the polymer beads are not respirable and do not represent a toxicological hazard, any dusts formed may represent an explosive hazard as do other organic dusts. Dust formation should be minimized. After manufacture, the polymer is included in the article and there is little likelihood of exposure.

If the polymer melt is overheated or in case of fire, pyrolysis products including hydrogen cyanide, acrylamide and carbon monoxide will be released. Suitable protective equipment should be worn by emergency services personnel. Maintenance workers cleaning extraction ducting and piping have a greater potential for exposure via the skin. Protective equipment should be worn.

There will be significant public contact with consumer products containing the notified polymer. However, due to the method of manufacture, the polymer will be tightly bound in a polymer matrix, and as a result public exposure to the free polymer is predicted to be low. The specific type of product available to the public which contains the polymer is not known. In addition, due to the high molecular weight of the polymer, minimal absorption of any free polymer through the skin is anticipated. The impurities, some of which are known to be hazardous are present at low concentrations. Furthermore, these impurities are encapsulated in the polymer matrix and the mobility of these impurities is predicted to be extremely low, and public exposure is expected to be negligible. Due to the low vapour pressure of the polymer, exposure through inhalation of the polymer is predicted to be low.

Disposal of the vapour condensates will be carried out on a case by case basis. In the worst case scenario, the vapours would be released into the atmosphere, causing a dilution of the gases, and as a result, minimal public exposure to the vapours is predicted.

#### 13. RECOMMENDATIONS

The following guidelines and precautions should be observed when using SR91B:

- . Where transfer of beads or pellets occurs, dust should be minimized with local exhaust ventilation. Areas in which the polymer melt is being formed should have good general ventilation. Exposure standards for acrylonitrile, alphamethylstyrene and styrene (2) should be observed strictly.
- . If exposure standards for acrylonitrile, alphamethylstyrene or styrene are exceeded then a respirator protecting against organic vapours and acid gases and conforming with AS 1716-1991 (3) should be worn.
- . Workers handling the notified chemical should wear long-sleeved overalls conforming with Australian Standard (AS) 3765.1-1990 (4) and eye protection conforming with AS 1337-1984 (5).
- . Workers who may be exposed to fume of monomers should wear neoprene gloves conforming with AS 2161-1978 (6).
  - Full face shields which conform with AS 1337-1984 should be used when cleaning fume condensates from equipment or when removing an extruder die-face.
- For cleaning operations a class L or class M dust respirator conforming with AS 1716-1991 (3) is required.
- . Vacuum hoods should be cleaned frequently to prevent accumulation of processing vapour condensates and appropriate methods for the disposal of these condensates should be employed.
- . Workers handling SR91B and reformulated products containing the chemical should have access to material safety data sheets.
- . The notified chemical should be stored in a dry place away from sources of heat.

## 14. MATERIAL SAFETY DATA SHEET

The Material Safety Data Sheet (MSDS) for SR91B (Attachment 1) was provided in Worksafe Australia format (7). This MSDS was provided by GE Plastics as part of their notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of GE Plastics.

# 15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals* (*Notification and Assessment*) Act 1989 (the Act), secondary notification of SR91B 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) Sax, Irving and RJ Lewis: Dangerous Properties of Industrial Materials, 7th edition van Nostrand Reinhold, NEW YORK, 1989.
- (2) Exposure Standards for Atmospheric Contaminants in the Occupational Environment. Guidance Note [NOHSC: 3008 (1991)]; National Exposure Standards [NOHSC: 1003 (1991)], 3rd Edition, October 1991.
- (3) Australian Standard 1716-1991 Respiratory Protective Devices, Standards Association of Australia Publ, Sydney 1991.
- (4) 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.
- (5) Australian Standard 1337-1984 Eye Protectors for Industrial Applications, Standards Association of Australia Publ, Sydney 1984.
- (6) Australian Standard 2161-1978 Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves), Standards Association of Australia Publ, Sydney 1978.
- (7) Guidance Note for Completion of a Material Safety Data Sheet. [NOHSC: 3001 (1991)], 3rd Edition, October 1991.