File No: NA/688

June 1999

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Tuftone HB-580 / Tuftone HB-688 / Tuftone HB-308

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

Tuftone HB-580 / Tuftone HB-688 / Tuftone HB-308

1. APPLICANT

The Sharp Corporation of Australia Pty Ltd of 1 Huntingwood Drive, Huntingwood, NSW 2148 has submitted a limited notification statement in support of their application for an assessment certificate for the polymer in Tuftone HB-580 / Tuftone HB-688 / Tuftone HB-308.

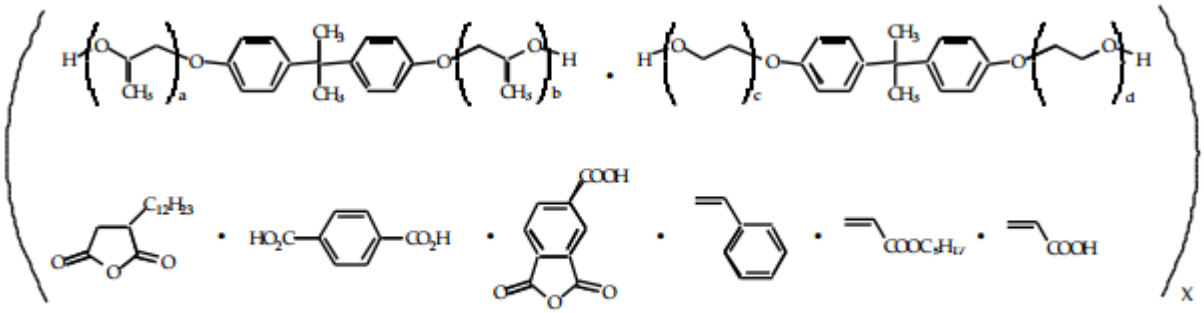
2. IDENTITY OF THE CHEMICAL

Chemical Name:	1,4-benzenedicarboxylic acid, polymer with 1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid, dihydro-3-(tetrapropenyl)-2,5-furandione, ethenylbenzene, 2-ethylhexyl-2-propenoate and α,α'-[(1-methylethylidene)-di-4,1-phenylene] bis [ω-hydroxypoly (oxy-1,2-ethanediyl)], α,α'-[(1-methylethylidene)-di-4,1-phenylene] bis [ω-hydroxypoly [oxy(methyl-1,2-ethanediyl)]] and 2-propenoic acid, graft, bis (1-methyl-phenylethyl) peroxide-initiated
Chemical Abstracts Service (CAS) Registry No.:	149367-99-7
Trade Names:	Tuftone HB-580, Tuftone HB-688, Tuftone HB-308
Number-Average Molecular Weight (NAMW):	2850
Weight-Average Molecular Weight:	40,020
Maximum Percentage of Low Molecular Weight Species	
Molecular Weight < 500:	4.03
Molecular Weight < 1 000:	9.36

Molecular Formula:

$(C_3H_6O)_aC_{15}H_{16}O_2 \cdot (C_2H_4O)_cC_{15}H_{16}O_2 \cdot C_{16}H_{26}O_3 \cdot C_8H_6O_4 \cdot C_9H_4O_5 \cdot C_8H_8 \cdot C_{11}H_{20}O_2 \cdot C_3H_4O_2$

Structural Formula:



a , b , c , d = 1~1.5

Weight Percentage of Ingredients:

Chemical Name	*CAS No.*	*Weight %*
1,4-benzenedicarboxylic acid (terephthalic acid)	100-21-0	5-25
1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid (4-carboxyphthalic anhydride)	552-30-7	0.5-15
dihydro-3-(tetrapropenyl)-2,5-furandione (tetrapropenyl succinic anhydride)	26544-38-7	0.5-15
ethenylbenzene (styrene)	100-42-5	10-40
2-ethylhexyl-2-propenoate (2-ethylhexyl acrylate)	103-11-7	1-10
α,α'-((1-methylethylidene) di-4,1-phenylene) bis (ω-hydroxypoly(oxy-1,2-ethanediyl)) (bisphenol A bis(polyethyleneglycol) ether)	32492-61-8	0.5-25
α,α'-((1-methylethylidene) di-4,1-phenylene) bis (ω-hydroxypoly (oxy(methyl-1,2-ethanediyl))) (bisphenol A bis(polypropyleneglycol) ether)	37353-75-6	20-60
2-propenoic acid (acrylic acid)	79-10-7	0.1-10
bis (1-methyl-1-phenylethyl) peroxide (dicumyl peroxide)	80-43-3	0.1-10
dibutyltin oxide	818-08-6	0.1-0.5

Method of Detection and Determination: data from gel permeation chromatography and infrared spectroscopy were provided for the notified polymer

Spectral Data: IR major characteristic peaks at 555, 691, 826, 1111, 1239, 1457, 1507, 1600, 1726 and 2929 cm^{-1}

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa: pale yellow powder

Particle Size: 9.2% by mass is smaller than 75µm

Particle size range (µm)	% w/w
>400	50.3
125-400	33.8
75-125	6.7
30-75	8.1
10-30	1.1
<10	0

Melting Range: 88-155°C

Glass Transition Temperature: 55-65°C (from Material Safety Data Sheet)

Specific Gravity: 1.12

Vapour Pressure: 1.7 x 10^{-10} kPa at 25°C

Water Solubility: <1mg/L at 20°C

Partition Co-efficient (n-octanol/water): no data presented; see comments below

Hydrolysis as a Function of pH: no data presented; see comments below

Adsorption/Desorption: no data presented; see comments below

Dissociation Constant: no data presented; see comments below

Flash Point: not applicable; chemical is a solid at room temperature

Flammability Limits: the notified chemical is not regarded as flammable, but is combustible

Autoignition Temperature: no self ignition before melting

Explosive Properties: no explosive properties (when subjected to thermal and mechanical sensitivity testing)

Reactivity: no oxidising properties

Comments on Physico-Chemical Properties

Tests were performed according to the EC Directive 92/69/EEC (European Commission, 1992) and OECD test guidelines (OECD, 1981), at Huntingdon Life Sciences Ltd, Eye, Suffolk, England, except for the vapour pressure estimation which was carried out at the Department of Physical Chemistry, The University of Leeds, Leeds, England. These facilities comply with UK Principles of Good Laboratory Practice. A report detailing all the tests performed was submitted.

Tests for n-octanol/water partitioning, hydrolysis, soil adsorption/desorption and dissociation were considered impractical for the notified polymer, due to its low solubility in water (<1mg/L) and *n*-octanol (<10mg/L), as well as the lack of a suitable substance specific analytical method. These data gaps were accepted because :

- hydrolysis of the ester and ether linkages of the polymer would not be expected under environmental conditions;
- on the basis of the polymer's low water solubility it is likely to have a high log P and to adsorb to, or be associated with, soil/sediment and organic matter and be immobile in soil; and
- the polymer contains a small amount of free carboxylic acid functionalities expected to have typical acidity.

4. PURITY OF THE CHEMICAL

Degree of Purity: 97% w/w (95-100%)

Non-hazardous Impurities (> 1% by weight):

Chemical name:	α,α'-((1-methylethylidene) di-4,1-phenylene) bis (ω-hydroxypoly(oxy(methyl-1,2-ethanediyl))
Synonyms:	bisphenol A bis(polypropyleneglycol) ether
Weight percentage:	3.1 (range 1-5)
CAS No.:	37353-75-6

Comments: may cause skin and eye irritation (from MSDS)

Notes:

This impurity also represents the maximum residual monomer content.
There are no toxic or hazardous impurities in the chemical.
From the list of polymer ingredients (i.e. presented in section 2), the following have been included on the National Occupational Health and Safety Commissions *List of Designated Hazardous Substances* (NOHSC, 1994a) :

1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid
ethenylbenzene
2-ethylhexyl-2-propenoate
2-propenoic acid
bis (1-methyl-1-phenylethyl) peroxide .

All are used up during the synthesis of the notified polymer, leaving a non-hazardous product.

Additives/Adjuvants: none

5. USE, VOLUME AND FORMULATION

The notified chemical is a polyester/styrene-acrylic grafted polymer and will be used in the printing industry as a binder resin of toner in printers and copiers. It will be imported into Australia as a component (50-55% and < 2% by weight) of formulated toner and developer products, in 100g cartridges and 700g bottles. The amounts that will be imported over the next five years are as follows :

1999	3.2 tonnes
2000	6.5 tonnes
2001	8.0 tonnes
2002	8.2 tonnes
2003	7.9 tonnes .

All manufacturing, formulation and packaging of the toner will be performed prior to importation.

6. OCCUPATIONAL EXPOSURE

The notified polymer is a component the imported toner product, which is also in powder form. Boxes of toner will be transported by road for distribution to customers in the printing industry. No reformulation or repackaging will take place. Hence, no exposure to the notified polymer, or toner, is expected during transportation and storage.

Occupational exposure to the notified polymer in Australia will primarily concern two main worker categories. These are printer/cpier service personnel and printing staff using printers and copiers.

Duties of the service personnel (approximately 800) will include cleaning the inside of the machine (particularly the exterior of the processing unit), servicing the machine (particularly

the exterior of the processing unit), servicing the machine and replacement of copier developer. The notifier estimated total exposure time foe an individual to be 47 hours per year, based on 187 services and 0.25 hours per service. Both inhalation and dermal exposure to the toner powder may occur during these activities. Service personnel may ear protective gloves, generally of the Latex disposal type.

Printing and/or office staff (approximately 450) will replace the used toner. To change the toner cartridge of printers, the seal tape is removed and then the cartridge is placed into the machine. During printing, the toner will be transferred on to the paper and heat-cured. Since toner is loaded directly into a laser printer or plane paper copier when required, the process is quick, taking approximately one minute. Toner addition/replacement would be required once a month on average. The estimated total exposure time for an individual worker to replace the toner is 12 minutes per year per machine. As a toner container is sealed, the operator would not be exposed at any toner until the seal tape is removed

Inhalation and dermal exposure to the toner powder may occur during toner replacement, particularly in the event of a container leak or spill. Printing and office workers would not normally wear protective equipment.

Exposure may occur upon handling printed matter. However, less than 50mg of toner is used per sheet of paper and it would not be separately available for exposure or dermal uptake as it is fused and fixed to the printed surface. These considerations indicate there would be no human exposure to the notified chemical during the handling of printed materials.

7. PUBLIC EXPOSURE

Public contact will only occur from touching the fixed toner on paper. The notifier states that the toner is fused to the paper and, under normal conditions, release from the surface is unlikely to occur. Consequently, the potential for public exposure to the notified polymer during all phases of its life cycle is considered to be negligible.

8. ENVIRONMENTAL EXPOSURE

Release

The notified polymer, as a component of a pre-formulated toner, will be imported in cartridges and bottles. Under normal use the toner is transferred onto a sheet of paper where it is firmly fixed to the surface by heat. Thus the polymer will be fixed into the cured toner and release to the environment will be negligible. Waste paper containing the toner (and thus the notified polymer) will eventually be sent to landfill, recycled or incinerated.

Release of the notified chemical will also occur through the disposal of cartridges and botles to lanfill, which would be widespread across Australia. The notifier has indicated that 1 g (i.e. 0.15%) of residue will be left in a toner cartridge. This equates to 0.1 g of toner remaining in a

spent cartridge. However, between 1 to 5% is a more realistic estimate of the amount of residue remaining in a cartridge (i.e. 1-5 g). Assuming this to be the upper limit of toner residue remaining in the cartridge, then the maximum quantity of polymer released in this manner would be 2.5 to 2.75 g per cartridge, representing 220 to 231 kg of the notified polymer per year.

In addition to this amount the notifier indicates that approximately 10% (i.e. 10 g from each cartridge) of the toner loaded into the photocopier is sent to a waste toner bottle, which is removed by the maintenance technician. The quantity of polymer released via this route would be 5 to 5.5 g per cartridge, representing a maximum of 440 to 462 kg per year.

Assuming an annual import of 8.2 tonnes of the notified polymer per year, the maximum quantity of polymer released ue to the disposal of used cartridges and waste bottles to landfill will be 660 to 693 kg per year.

Environmental release during transport due to accidental spillage will be limited because the toner is supplied in small volume cartridges.

Environmental exposure to the notified polymer could occur during disposal or recycling of paper containing the polymer (see below).

Fate

The polymer will most likely share the fate of its paper substrate and be recycled or disposed of via landfill or incineration. The small quantities of residual toner in spent containers will also be disposed of by landfill. Polymer disposed of to landfill is unlikely to leach or contaminate surface water because of its low water solubility and expected high partition coefficient.

Paper recycling is a growing industry in Australia. Waste paper is repulped using a variety of alkalis, water emulsifiable organic solvents and dispersing, bleaching and wetting agents to enhance the fibre separation, ink detachment from the fibres and pulp brightness and the whiteness of the paper. After pulping, the contaminants and the ink are separated from the fibres by pumping the stock through various heat washing, screening, cleaning, flotation and dispersion stages. The notifier has provided no data on the likely behaviour of the polymer during the recycling process. The hydrolysis of ester linkages under alkaline conditions will be minimal due to the low solubility of the polymer. The polymer therefore is likely to survive the paper recycling conditions, either remaining bound to the pulp or becoming associated with the sludge. In the latter case, the polymer will arrive in landfill where it can be expected to remain intact, or be destroyed through incineration.

Biological membranes are not permeable to polymers of very large molecular size and therefore bioaccumulation of the notified polymer is not expected (Gobas *et al.*, 1986; Anliker *et al.*, 1988).

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicological data were provided for the notified polymer. This is acceptable for polymers of number-average molecular weight (NAMW) of greater than 1000 daltons.

However according to the Material Safety Data Sheet (MSDS) for AR-330ND/330SD/330DV black developer and AR-330NT/330ST/330T black toner which are similar products were shown to be non mutagenic when tested *with Salmonella typhimurium* and *Escherichia coli* in the Ames test and an acute oral toxicity of LD_{50} > 5 000 mg/kg and acute inhalation toxicity of LC_{50} > 6.42 mg/L.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were provided for the notified polymer. This is acceptable for polymers of number-average molecular weight (NAMW) of greater than 1000 daltons.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

The majority of notified polymer should not enter the environment until it is incorporated into the heat-cured toner matrix and fixed to paper. Disposal of the waste paper containing the toner would normally occur through landfill, recycling or incineration. In landfill the toner (and thus the notified polymer) should remain fixed to the paper substrate and remain immobile. Incineration products of the notified polymer should not produce an environmental hazard. After recycling, the toner will either remain bound to the pulp or become associated with sludge. The sludge would be destined to landfill where the toner could persist but remain bound to the sludge and immobile..

Accidental spillage of the polymer, either during replacement of cartridges or during transport, should result in powder wastes being sent to either landfill or incineration facilities. Spent cartridges containing residues of toner are likely to be sent to landfill. As a worst case, a maximum of 693 kg of the notified polymer could be sent to landfill at maximum import quantities. The disposal of cartridges would be widespread across Australia.

The notified polymer is not likely to present a concern to the environment when it is stored, transported and used in the proposed manner because the environmental exposure and the overall environmental hazard should be negligible.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

There is no toxicological data available on the notified polymer. However, the notifier has determined that neither the notified polymer, nor the toner, would be a hazardous substance, under the National Occupational Health and Safety Commissions *Approved Criteria for*

Classifying Hazardous Substances (NOHSC, 1994b). The MSDS for AR-330ND/330SD/330DV black developer and AR-330NT/330ST/330T black toner report toxicity data for a similar toner, namely very low acute oral toxicity (LD_{50} > 5 000 mg/kg) and acute inhalation toxicity (LC_{50} > 6.42 mg/L) and a negative Ames test.

The particle size of the notified polymer is above the respirable range (i.e. all particles are >10μm in size). However, approximately 20-25% w/w of particles are within the inspirable range (<180μm) and may be lodged in the upper respiratory tract and lead to respiratory irritation. The main residual monomer of the notified chemical may cause skin and eye irritation. However, as it is not a hazardous substance and is present in the polymer preparation at 3.1%, it is unlikely to be a source of irritation in the imported toner product.

Occupational Health and Safety

Toner powder containing the notified polymer will be used by industrial printing firms. Training on how to handle the process unit and toner cartridge/bottle (containing the notified polymer) will be given to all personnel concerned. To date there are no records of injuries or diseases related to workers exposed to the test substance.

Service personnel (approximately 800) may be exposed to the notified polymer when cleaning printer/copier equipment and replacing copier developer; however, as the notified polymer or the toner product is not hazardous, the risk of adverse health effects is low. Disposable gloves may be worn to prevent skin irritation and workers should avoid any generation of dust when handling the toner.

Printing staff (approximately 450), who will perform additions of toner and replacement of a used toner container (cartridge or bottle), are expected to be exposed infrequently to the notified polymer as the toner container is sealed and loaded directly into a printing machine. Upon application to the paper, the toner is fused to the surface and release is unlikely to occur. Therefore, the risk of adverse health effects to printing personnel is very low and no protective equipment is required. Nevertheless, any generation of dust should be avoided.

Spilt residues should be swept up manually or using an industrial vacuum cleaner and placed within a waste container.

Given these considerations, the chemical will not pose a significant health hazard in the occupational environment.

Workers handling printed paper are not at risk of adverse health effects because the polymer is fixed to the paper and not available for exposure or dermal uptake.

There is a NOHSC exposure standard for carbon black, a component in the imported product. Employers are responsible for ensuring that the exposure standard (3 mg/m^3, time weighted average), is not exceeded in the workplace.

Public Health

Based on its use pattern, physico-chemical properties and low toxicity, the notified polymer will not pose a significant hazard to public health.

13. RECOMMENDATIONS

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

- Avoid generation of dust clouds when handling the toner;
- Service operators should wear disposable, rubber gloves when handling toner;
- Spillage of the notified chemical should be avoided. Spillages should be cleaned up promptly with absorbents which should be put into containers for disposal;
- Good personal hygiene should be practised to minimise the potential for ingestion;
- A copy of the appropriate MSDS should be easily accessible to employees .

The NOHSC exposure standard for carbon black should not be exceeded in the workplace.

14. MATERIAL SAFETY DATA SHEET

The MSDS for Tuftone HB-580, AR-330NT/330ST/330T (black toner) and AR-330/330SD/330DV (black developer) were provided in a format consistent with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994c).

These MSDS were 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. No other specific conditions are prescribed.

16. REFERENCES

Anliker R, Moser P and Poppinger D (1988) Bioaccumulation of dyestuffs and organic pigments in fish. Relationships to hydrophobicity and steric factors. *Chemosphere* **17(8)**, 1631-1644.

European Commission (1992) *Methods for the Determination of Physico-Chemical Properties, Part A, Commission Directive 92/69/EC.* Official Journal of the European Communities No. L383A, December 1992.

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