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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

STYRENE-ACRYLATE COPOLYMER

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

STYRENE-ACRYLATE COPOLYMER

1. IMPORTER

Canon Australia Pty Ltd, 1 Thomas Holt Drive, North Ryde, NSW 2113

2. IDENTITY OF THE CHEMICAL

Trade name: Styrene-acrylate copolymer

Maximum percentage of low molecular weight species (molecular weight < 1000): 2.5%

Maximum content of residual monomers: <0.1% (w/w)

3. PHYSICAL AND CHEMICAL PROPERTIES

Styrene-acrylate copolymer is a transparent, non-volatile powder at room temperature and atmospheric pressure with a slight plastic odour. Its physical and chemical properties include:

Glass-transition temperature: 55-65°C

Density: 1000-1200 kg/m^3

Pyrolysis products: on combustion of the polymer, carbon dioxide and toxic fumes such as carbon monoxide may be emitted.

Water solubility: < 10^{-3}g/L

Degree of hydrolysis at pH=1-2 or pH=4-9 (25°C): stable, <2% degradation over 2 weeks @ 40°C and pH=1.2-9.0

4. METHOD OF DETECTION AND DETERMINATION

Styrene-acrylate copolymer is a constituent of a toner product. Airborne toner particulates can be sampled on appropriate filters in accordance with Australian Standard AS 3640-1989(1). The polymer constituents can be extracted in organic solvents such as

toluene and xylene, and then separated by gel permeation chromatography (GPC) and identified by infra-red spectrophotometry.

5. PURITY OF THE CHEMICAL

Degree of purity: more than 99% (w/w)

Toxic or hazardous impurities: less than 0.1% (w/w)

(Note: the impurities represent a mixture of residual monomers which generally have low acute oral and inhalational toxicities in test animals but are slight to moderate irritants to the eyes and skin. However, these impurities present at an overall concentration of less than 0.1% by weight of the polymer are unlikely to pose a serious health hazard.)

6. INDUSTRIAL USES

Styrene-acrylate copolymer is intended to be used exclusively as a binder resin in toner products such as the P170 Toner for photocopying and laser beam printing. Incidentally, the P170 Toner will contain 45-55% by weight of the styrene-acrylate copolymer. Other ingredients of the P170 Toner are iron oxide (CAS No.: 1317-61-9) and amorphous silica, fumed (CAS No.: 7631-86-9).

The estimated quantity of the copolymer to be imported into Australia is 1-10 tonnes for the first year and between 10-100 tonnes for each of the following four years.

7. PUBLIC AND OCCUPATIONAL EXPOSURE

The formulated P170 Toner will be imported into Australia in tape-sealed cartridges which are ready to use in photocopiers and laser beam printers. Only the seal-tape of the cartridge needs to be opened immediately before use. No reformulation, packaging, bottling, filling or refilling of containers needs to be carried out in Australia. After use, the formulated product will be fused to paper in a water insoluble matrix. Therefore, it can be expected that there will be very low public and worker exposure to the copolymer and the toner product under normal use conditions.

However, photocopier maintenance workers who frequently come into direct contact with the toner powder will have higher exposure through skin contact and inhalation.

8. ENVIRONMENTAL EXPOSURE

8.1 Release

As the formulated toner will only be used for office photocopying and laser beam printing, it is expected that only a negligible amount of toner waste would be generated or released to the environment.

8.2 Fate

The quantity of waste toner that will need to be incinerated or disposed of in a landfill is expected to be very small.
Paper to which the polymer is fixed will ultimately be incinerated, disposed of in a landfill, or recycled. When incinerated, the polymer will be degraded to oxides of carbon. When disposed in a landfill, because of its high molecular weight, the polymer should not readily biodegrade and, therefore, is likely to persist.
(Note: generally, polymers need to be reduced to a molecular weight of 500 before biodegradation can occur(2).) Given its low water solubility, the polymer is expected to have low mobility in landfill sites.

Wastepaper is usually repulped in a pulper which utilises a number of alkalis, dispersing agents, wetting agents, water emulsifiable organic solvents and bleaching agents. These chemicals enhance fibre separation, ink detachment from the fibres, pulp brightness and 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(3).

In general the recycling of paper is likely to create a situation where the polymers attached to the paper may degrade and become more soluble. However, in the present case given the stability of styrene-acrylate copolymer to hydrolysis, it is unlikely that this polymer will degrade under the recycling conditions. Due to its low water solubility and resistance to hydrolysis, the polymer may either remain associated with the pulp or if separated (dependent on the conditions) with the sludge.

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Absorption

The key factors which appear to determine absorption of a chemical by an organism are its molecular weight and lipophilicity. It is generally believed that as molecular weight increases, absorption decreases. Although it is not possible to identify any single molecular weight limit above which no absorption will occur, the available information suggests that substances with molecular weights greater than 400 are generally not readily absorbed through the intact skin and that substances with molecular weights greater than 1000 are generally not readily absorbed through the intact gastrointestinal tract(4).

Given its high molecular weight and polydispersity (maximum percentage of low molecular weight species molecular weight < 1000 = 2.5%), it is believed that the styrene-acrylate copolymer would not be readily absorbed through the intact skin and gastrointestinal tract, and therefore, should not pose a significant acute toxicity risk.

9.2 Acute Toxicity

9.2.1 Oral Toxicity

A limit test was carried out in a group of 5 male and 5 female CD rats, in which a 5000mg/kg dose of a toner product (which contained a polymer similar to the styrene-acrylate copolymer) was administered in corn oil by gavage. None of the animals died and no significant clinical symptoms were observed within 14 days of the treatment. Gross necropsy showed no macroscopic pathological changes. The oral LD_{50} was greater than 5000mg/kg for the similar product(5).

9.3 Mutagenicity

9.3.1 *Salmonella typhimurium* histidine reversion assay

Styrene-acrylate copolymer and the P170 Toner (which contained 45-55% by weight of the styrene-acrylate copolymer) were tested separately for mutagenicity in *Salmonella typhimurium* TA98 and TA100 strains, both in the presence and absence of an exogenous mammalian metabolic activation system. In both tests, a positive dose-response relationship or a significant increase in the mean

number of revertant colonies per plate was not demonstrated in either of the two strains, in the presence or absence of an activating system. These results indicate that under the test conditions, styrene-acrylate copolymer and the P170 Toner were not mutagenic in *Salmonella typhimurium*(6,7).

9.4 Overall Assessment of Toxicological Data

The Toner is likely to exhibit very low acute oral toxicity, as a similar product exhibited an acute oral toxicity (LD_{50}) of greater than 5000mg/kg in rats.

No irritation tests have been presented for the copolymer. However, because of its physical form as a fine powder, it is expected that the styrene-acrylate copolymer may irritate the eyes and upper respiratory tract.

Due to its low potential for absorption, the copolymer is expected to pose a minimal systemic toxicity. Also coupled with its predicted low irritation potential, the polymer is not likely to present an acute toxicity hazard.

Both styrene-acrylate copolymer and the P170 Toner were not genotoxic in *Samonella typhimurium*.

10. ENVIRONMENTAL ASSESSMENT

10.1 Assessment of Environmental Effects

Due to its high molecular weight and small proportion of low molecular weight species, the polymer is likely to be of low bioavailability. Therefore, it is expected that the polymer will have low toxicity to soil flora and fauna.

10.2 Assessment of Environmental Hazards

From its low environmental exposure as a result of normal use and its predicted low toxicity to soil flora and fauna, the polymer should pose a low environmental hazard.

Environmental exposure to the polymer could occur through two main routes: when paper containing the polymer is recycled; and when such paper is disposed in a landfill. The quantity of polymer that will be fixed to paper as a result of photocopying and laser beam printing may be significant after the first year of importation

(maximum of 100 tonnes per annum). However, because of the low water solubility of the polymer and its resistance to hydrolysis, the environmental exposure to the polymer or to its degradation products resulting from landfill desposition or recycling is likely to be low.

Accidental spillage of the polymer should also result in negligible hazard to the environment, given its physical state as a solid and low water solubility.

11. Assessment of public and Occupational Health and Safety Effects

Public and worker exposure to the styrene-acrylate copolymer and P170 Toner is likely to be minimal under normal use conditions. From its predicted low acute oral toxicity and low irritating potential to the eyes and upper respiratory tract, exposure to both the copolymer and P170 Toner should not pose a significant acute health and safety hazard to the public and workers.

12. RECOMMENDATIONS FOR THE CONTROL OF PUBLIC AND WORKER EXPOSURE

To minimise public and worker exposure to the toner products, in general the following guidelines and precautions should be observed:

. as a good work practice, photocopiers and laser beam printers should be located in a well ventilated area to control the accumulation of any dusts, gases or fumes;

. a copy of the Material Safety Data Sheet should be made available to all personnel who may have exposure to the toner; and

. photocopier and printer maintenance workers who frequently come into direct contact with the toner powder should:

  - wear appropriate gloves (for example, cotton or impervious gloves);

  - avoid the generation of a dust cloud; and

  - observe good personal hygiene practices at work.

Note: guidance on the general working practices associated with the operation of office copying machines are available in Worksafe Australia *Guide on Office Copying Machines*(8).

13. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Industrial Chemicals (Notification and Assessment) Act 1989 (the Act), secondary notification of the styrene-acrylate copolymer shall be required by Canon Australia Pty Ltd if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

14. REFERENCES

(1) Standards Australia, AS 3640-1989 *Workplace Atmospheres - Method for Sampling and Gravimetric Determination of Inspirable Dust*, Standards Australia, Sydney, 1989.

(2) Chemical and Engineering News, Vol 68, 26, p.13, 1990

(3) Forestry Canada, Industry/Trade and Technology Directorate and Environment Canada, Final Report, *Waste Paper Study (to end of 1989)*, p.56-57.

(4) United States Federal Register, 40 CFR Part 723, *Premanufacture Notification Exemptions; Exemptions for Polymers,* 1984

(5) Acute Oral Toxicity to Rats of NK-34, Data on File, Canon Inc. Japan, 891050D/CNN 9/AC, October, 1989.

(6) Report of Mutagenicity Test Using Microorganisms, Data on File, Canon Inc Japan, Report No.415, October, 1990.

(7) Report of Mutagenicity Test Using Microorganisms, Data on file, Canon Inc Japan, Report No.416, October, 1990.

(8) National Occupational Health and Safety Commission, *Office Copying Machines*, AGPS, Canberra, December, 1989