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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

POLYMER OF 2-PROPENOIC ACID, BUTYL ESTER, DIETHENYLBENZENE, AND ETHENYLBENZENE

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Director
Chemicals Notification and Assessment

Full Public Report

POLYMER OF 2-PROPENOIC ACID, BUTYL ESTER, DIETHENYLBENZENE, AND ETHENYLBENZENE

1. IMPORTER

Kodak Australasia Pty Ltd, 173 Elizabeth Street, Coburg, Victoria. 3058.

2. IDENTITY OF THE CHEMICAL

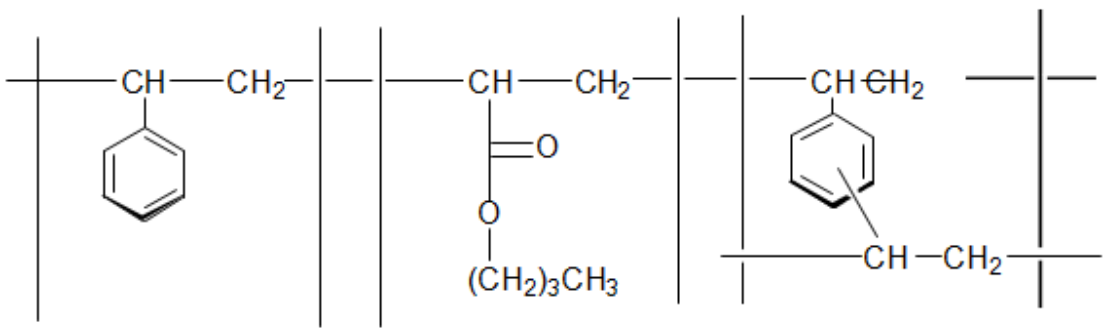
Chemical name: Polymer of 2-propenoic acid, butyl ester, diethenylbenzene, and ethenylbenzene

Chemical Abstract Service (CAS) No. 57516-68-4

Other name: Styrene acrylate copolymer

Empirical formula: $(C_{10}H_{10}.C_8H_8.C_7H_{12}O_2)_n$

Structural formula:



Number-average molecular weight: 32,700

Weight-average molecular weight: 115,000

Maximum percentage of low molecular weight species (molecular weight < 1000): 0%

Monomers:

. **Identity:** Ethenylbenzene
Synonym: Styrene
CAS No.: 100-42-5
Weight percentage: 76.8%

. **Identity:** 2-Propenoic acid, butyl ester
Synonym: Butyl acrylate
CAS No.: 141-32-2
Weight percentage: 22.9%

. **Identity:** Diethenylbenzene
Synonym: Benzene, divinyl
CAS No.: 1321-74-0
Weight percentage: 0.3%

Maximum content of residual monomers: <0.2% (w/w)

3. PHYSICAL AND CHEMICAL PROPERTIES

Styrene acrylate copolymer consists of fine white beads at room temperature and atmospheric pressure. Its physical and chemical properties include:

Glass-transition temperature: 56.7-64.8°C

Vapour pressure: negligible; the chemical is a cross-linked polymer

Water solubility: negligible; the chemical is cross-linked polymer

Explosion potential: this material, like most organic materials in powder form, is capable of creating a dust explosion

Reactivity: incompatible with strong oxidisers

Particle size distribution: range: 63-116 microns

The notifier has justified the lack of test results for hydrolysis, partition coefficient and soil adsorption on the grounds that the notified substance is a high molecular weight, cross linked polymer with negligible vapour pressure and water

solubility. This is acceptable for the proposed level of importation.

4. METHOD OF DETECTION AND DETERMINATION

Styrene acrylate copolymer will be used as a binder in commercial photocopier formulations. The copolymer can be extracted in organic solvents such as toluene and xylene, then separated by size exclusion chromatography and identified by infra-red spectrophotometry.

5. PURITY OF THE CHEMICAL

Degree of purity: 99-100%
Toxic or hazardous impurities:

.Identity: benzene, ethenyl-
Synonym: styrene
CAS No.: 100-42-5
Maximum residual: 0.1%
Toxic properties: moderate acute oral toxicity (mice LD_{50}=316mg/kg); very low inhalational toxicity (rat LC_{50}=24g/m^3/4 hr); mild skin irritant (rabbit); mild eye irritant (rabbit)(1,2)
National exposure standards(3):
- TWA : 50ppm
- STEL: 100ppm

.Identity: 2-propenoic acid, butyl ester
Synonym: butyl acrylate
CAS No.: 141-32-2
Maximum residual: 0.025%
Toxic properties: moderate acute oral toxicity (rat LD_{50}=900mg/kg); very low inhalational toxicity (rat LC_{50}=2730ppm/4 hr); mild skin irritant (rabbit); mild eye irritant (rabbit); (1,2)
National exposure standards(3):
- TWA : 10ppm; Sensitiser(4)

. **Identity:** Pentanenitrile
Synonym: n-Valeronitrile
CAS No.: 110-59-8
Maximum residual: 0.05%
Toxic properties: moderate acute oral toxicity (mice LD_{50}=191mg/kg) (2)

(Note: these impurities are present at an overall concentration of less than 0.2% by weight of the polymer and are unlikely to pose a serious health hazard.)

Additives/Adjuvants:

Identity: Silica
CAS No.: 7631-86-9
Weight percentage: <1%
Toxic properties: low acute oral toxicity (rat LD_{50}=3160 mg/kg); this form of silica does not cause silicosis (1)

6. INDUSTRIAL USES

Styrene acrylate copolymer is to be used as a binder in commercial photocopier formulations, Kodak HX Developer and Kodak HX Toner. The HX Developer will contain 10-15% of the copolymer, together with 85-90% strontium ferrite (CAS No. 12023-91-5) and <1% carbon black (CAS No. 1333-86-4). The HX Toner will contain 90-95% copolymer, with 5-10% carbon black.

The formulations will be imported into Australia in sealed polyethylene cartridges, which will be placed in the photocopier by the customer. The formulations are mechanically applied to paper to produce a water insoluble polymer matrix, which is permanently fused to the paper. No reformulation, repackaging, filling or refilling of containers will be carried out in Australia.

It is estimated that less than 500 kilograms per year of the copolymer will be imported into Australia for the first three years.

7. PUBLIC AND OCCUPATIONAL EXPOSURE

It is expected that under normal use conditions, as described in Section 6, there will be very low public and worker exposure to styrene acrylate copolymer and its formulated products.

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

8. ENVIRONMENTAL EXPOSURE

8.1 Release

Minimal environmental release is expected to occur during normal use conditions, as described in Section 6. No spillage during use is anticipated as the polymer will be used in polyethylene cartridges. If spillage does occur, it should be swept up and disposed of by incineration or contract with a licensed waste disposal company. Empty cartridges will be returned to the US manufacturer for recycling or disposed of by contract with a licensed chemical waste disposal agency. All formulation and packaging will be carried out overseas.

Releases to the environment may occur through processing of waste paper.

8.2 Fate

Unless incinerated, the polymer is likely to arrive in landfill bound to waste paper. As such, it will be immobile, and no leaching from landfill would be expected despite the polymer's expected persistence.

Paper recycling is a growing industry in Australia. Wastepaper is repulped using a variety 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. The notifier has provided no data on the likely behaviour of the polymer during the recycling process. However, polymers of this

nature would be expected to survive the above conditions, either remaining bound to the pulp or becoming associated with the sludge. In the latter case, the polymer will either arrive in landfill where it can be expected to remain intact, or be destroyed through incineration.

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 (5).

Given its high molecular weight it is unlikely that styrene acrylate copolymer would be readily absorbed through the intact skin and gastrointestinal tract, and therefore, should not pose a significant acute toxicity risk.

9.2 Toxicological Data

No toxicological data for styrene acrylate copolymer was supplied.
However, a summary of the toxicity data for a structurally similar polymer, 2-propenoic acid, butyl ester, telomer with ,4-diethenylbenzene, 1-dodecanethiol and ethenylbenzene (CAS No. 67338-64-1) was provided by Kodak. The 1-dodecanethiol forms <1% of the polymer.

This polymer exhibited very low acute oral (LD_{50} rat/mouse >3200mg/kg) and dermal (LD_{50}>1000mg/kg) toxicity, and was only a slight skin (guinea pig) and eye irritant (rabbit). The compound was not a skin sensitiser (guinea pig) and, in a 16 day repeated dose oral toxicity study, rats fed up to 737mg/kg/day showed no significant toxicological effects. For more detailed information on these toxicity tests see Appendix 1.

9.3 Overall Assessment of Toxicological Data

Styrene acrylate copolymer has a low potential for absorption and is therefore expected to pose minimal systemic toxicity. This low absorption potential together with the predicted low irritation potential, suggest that the polymer is unlikely to present an acute toxicity hazard.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

10.1 Assessment of Environmental Effects

Environmetal effects testing is not required for small volume polymers, but limited data have been provided for a similar compound, a telomer (or, strictly speaking, a cotelomer) of the same three ingredients containing dodecanethiol (<1%) as chain-transfer agent. A telomer is distinguished from a polymer by the incorporation of a chain-transfer agent or telogen YZ, the two radicals of which, Y and Z, form the termini of the telomer. Telomers have much lower molecular weights than the corresponding polymer prepared without a chain-transfer agent (6). Thus the absence of any significant toxic characteristics for the telomer can be regarded as good evidence that the notified copolymer, with its higher molecular weight, will also have a low toxicological hazard.

Results of the environmental effects tests for the telomer are as follows:

Test	Test organism	Result
Acute oral	Rat/mouse	LD_{50}>3,200mg/kg
Acute	Fish	LC_{50}>100mg/L
Acute	Snails	LC_{50}>100mg/L
Acute	Flatworms	LC_{50}>100mg/L
Acute	Daphnids	LC_{50}=32mg/L
Germination/ root growth	Radish,lettuce,ryegrass	No effect at 100mg/L

Rodents were administered doses of test material by gavage as a 10% suspension in a vehicle composed of 0.5% guar gum in water. Aquatic studies were performed according to the procedure of Ewell et al (7) using acetone (0.5ml/L) as carrier solvent. Phytotoxicity was investigated using a method developed for water

soluble chemicals (8). While no toxic effects on plants or aquatic organisms were apparent, the results tabulated above should be treated with caution, as nominal rather than measured concentrations of the insoluble test material were used.

Styrene acrylate copolymer would not be expected to exhibit toxic characteristics because large polymers of this nature are not readily absorbed by biota.

10.2 Assessment of Environmental Hazards

The low environmental exposure of the polymer as a result of normal use and its expected low toxicological profile indicate that the overall environmental hazard should be negligible.

Environmental exposure to styrene acrylate copolymer could occur when paper containing the polymer is recycled or disposed of. In each case, the final destination is likely to be landfill where the polymer can be expected to persist but remain immobile, being either bound to paper or to the sludge form the recycling process.

Accidental spillage of the polymer should result in negligible hazard given that low water solubility and low toxicity are typical for a compound of this type, and it will be marketed in small packages.

11. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Public and worker exposure to styrene acrylate copolymer and its formulated products are likely to be minimal under normal use conditions, since the chemical is imported, distributed and supplied in sealed cartridges. The cartridge is designed to prevent user access and cartridge disposal is by incineration, or by contract with a chemical waste disposal agency.

From its predicted low absorption, toxicological and irritating potential, exposure to Styrene acrylate copolymer and the formulated products should not pose a significant acute health and safety hazard to the public and workers.

12. ASSESSMENT OF MATERIAL SAFETY DATA SHEETS

The Material Safety Data Sheets (MSDS) for styrene acrylate copolymer and the Toner and Developer formulated products are provided at Attachments 1, 2 and 3. These MSDSs were provided by Kodak Australasia Pty Ltd, in Worksafe Australia format, as part of their notification statement. They are reproduced here as a matter of record. The information and recommended control measures contained in these MSDSs generally reflect the hazards associated with use of the copolymer and its products. The accuracy of this information remains the responsibility of Kodak Australasia Pty Ltd.

13. RECOMMENDATIONS FOR THE CONTROL OF PUBLIC AND WORKER EXPOSURE

To minimise public and worker exposure to the Styrene acrylate copolymer and its toner and developer products, the following guidelines and precautions should be observed:

. as a good work practice, photocopiers 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 developer; and

. photocopier and printer maintenance workers who frequently come into direct contact with the toner and developer 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* (9).

14. REQUIREMENTS FOR SECONDARY NOTIFICATION

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

15. REFERENCES

(1) Sax N I & Lewis R J, *Dangerous Properties of Industrial Materials*, 7th edition, Volume 1-3, 1989.

(2) National Institute for Occupational Safety and Health (US), *Registry of Toxic Effects of Chemical Substances (RTEC)*, NIOSH, Cincinnati, Ohio, October 1985.

(3) National Occupational Health and Safety Commission, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment*, AGPS, Canberra, May, 1990.

(4) American Conference of Governmental Industrial Hygienists, *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 5th edition, Cincinnati, Ohio, 1986.

(5) Clayton G D & Clayton F E, *Patty's Industrial Hygiene and Toxicology*, third revised edition, Volume 2C, John Wiley & Sons, Inc., 1981.

(6) Gordon B & Loftus J E, *Enclycopedia of Polymer Science and Engineering*, Vol 16, 533-554.

(7) Ewell WS, Gorsuch J W, Kringle R O, Robillard K A & Spiegel R C, *Environmental Toxicology and Chemistry*, 1986, 5, 831-840.

(8) Gorsuch J W, Kringle R O & Robillard K A, *Plants for Toxicity Assessment, ASTM STP 1091*, Wang W, Gorsuch J W & Lower W R, Eds, American Society for Testing and Materials, Philadelphia, 1990, pp 49-58.

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

APPENDIX 1

Summary of Toxicity Testing for 2-propenoic acid, butyl ester, telomer with 1,4-diethenylbenzene, 1-dodecanethiol and ethenylbenzene (CAS No. 67338-64-1).

A summary of the toxicity data for a structurally similar polymer, 2-propenoic acid, butyl ester, telomer with 1,4-diethenylbenzene, 1-dodecanethiol and ethenylbenzene (CAS No. 67338-64-1) was provided by Kodak. The 1-dodecanethiol forms <1% of the polymer.

Acute oral toxicity

An acute oral toxicity study was carried out in groups of 4 male rats and mice. The animals were administered doses of 200, 400, 800, 1600 and 3200 mg/kg of the test material by gavage as a 10% suspension in a 0.5% guar gum vehicle. There were no abnormal clinical symptoms. Necropsies were not performed. The acute oral LD_{50} was greater than 3200 mg/kg in male rats and mice.

Acute dermal LD50 in guinea pigs

The test material was applied to the shaved abdomens of 3 guinea pigs under an occlusive wrap for 24 hours, at dose levels of 250, 500, 1000 mg/kg. Desquamation was noted at the site of application in all animals after one week, which persisted for two weeks at the 2 highest doses. Weight gains were normal, and there were no clinical signs. The acute dermal LD_{50} was greater than 1000 mg/kg in guinea pigs.

Dermal irritation in guinea pigs

A 33% suspension of test material in 10% ethanol and 90% glycerol was applied daily to the clipped dorsal area of guinea pigs for 10 days. Slight erythema was noted after the first application in 3 of the 5 guinea pigs. All animals showed minimal or spotty erythema following the last administration.

Eye irritation

Several crystals of the test material were placed in the conjunctival sac of the eye in each of 6 rabbits. In three of the animals treated, the eyes were immediately irrigated. The eyes were examined 1, 24 and 48 hours, and 14 days after dosing. One hour after administration, slight erythema of the conjunctivae and nictitating membranes in all 6 eyes, and slight oedema in one unwashed eye were observed, but all eyes were normal after 24 hours. Fluorescein testing at 24 hours revealed slight staining of the nictitating membrane in one of the unwashed eyes. All eyes were normal at 48 hours, and 14 days following treatment.

Skin sensitisation

A 1% suspension of the test material in Freund's adjuvant was injected into one footpad of each of 10 guinea pigs. Ten days later, a suspension of 1% of the test material in 80% dichloromethylene and 20% acetone, dioxane and guinea pig fat (7:2:1 ratio) was rubbed on the back skin of all animals. There was no response indicative of an allergic reaction after 24 and 48 hours.

Repeat dose studies

Groups of 5 male rats each received the test material with 2% corn oil in a commercial rodent diet at concentrations of 0, 0.1% and 1.0% for 16 days. Food consumption, bodyweight, haematology, organ weights, clinical chemistry, gross and microscopic pathology was performed at necropsy.

Bodyweights, food consumption, haematology, clinical chemistry, absolute and relative kidney weights, and gross and microscopic pathology were normal.