File No: **NA/7**
Date: 18 February 1991

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

POLYMER OF PENTANEDIOIC ACID, DIMETHYL ESTER; 1,4-BENZENEDICARBOXYLIC ACID, DIMETHYL ESTER; 1,2-PROPANEDIOL AND 1,2,3-PROPANETRIOL

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

POLYMER OF PENTANEDIOIC ACID, DIMETHYL ESTER;

1,4-BENZENEDICARBOXYLIC ACID, DIMETHYL ESTER;

1,2-PROPANEDIOL AND 1,2,3-PROPANETRIOL

1. IMPORTER

Kodak (Australasia) Pty Ltd, 173 Elizabeth Street, Coburg, VIC 3058

2. IDENTITY OF THE CHEMICAL

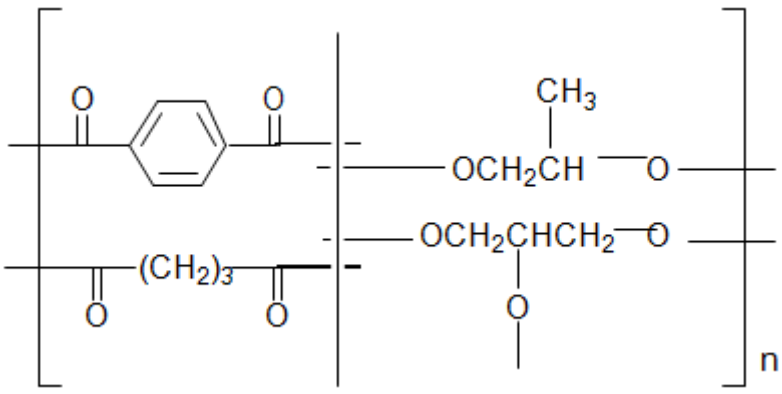
Chemical name: Polymer of pentanedioic acid, dimethyl ester; 1,4-benzenedicarboxylic acid, dimethyl ester; 1,2-propanediol and 1,2,3-propanetriol

Chemical Abstract Service (CAS) No.: 120611-31-6

Trade name: Polyester

Empirical formula: $(C_{10}H_{10}O_4 \cdot C_7H_{12}O_4 \cdot C_3H_8O_3 \cdot C_3H_8O_2)_n$

Structural formula:



Spectral data: Infrared spectrum (major absorption bands for identification at 1100, 1250 and 1725 cm^{-1})

Number-average molecular weight: 10000

Weight-average molecular weight: 64000

Maximum percentage of low molecular weight species (molecular weight < 1000): <0.02% (w/w)

Monomers:

.Identity: pentanedioic acid, dimethyl ester
CAS No.: 1119-40-0
Weight percentage: 6%

.Identity: 1,4-benzenedicarboxylic acid, dimethyl ester
Synonym: dimethyl terephthalate
CAS No.: 120-61-6
Weight percentage: 50%

.Identity: 1,2-propanediol
Synonym: propylene glycol
CAS No.: 57-55-6
Weight percentage: 42%

.Identity: 1,2,3-propanetriol
Synonym: glycerine; glycerol
CAS No.: 56-81-5
Weight percentage: 2%

Maximum content of each residual monomer: <0.5% (w/w)

3. PHYSICAL AND CHEMICAL PROPERTIES

"Polyester" is a white, non-volatile, crystalline powder at room temperature and atmospheric pressure. Its physical and chemical properties include:

Glass-transition temperature: 58-65°C

Stability:

. will begin to decompose at 350°C giving off carbon dioxide and toxic fumes such as carbon monoxide; and

. will depolymerise in the presence of heat (>100°C) and water.

Water solubility: < 1g/L (detection limit)

4. METHOD OF DETECTION AND DETERMINATION

"Polyester" is a constituent of a number of Kodak toner products. 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 methylene chloride, and then separated by size exclusion chromatography (SEC) and identified by infra-red spectrophotometry.

5. PURITY OF THE CHEMICAL

Degree of purity: more than 99.7% (w/w)

Toxic or hazardous impurities:

.Identity: 3,5-bis(1,1-dimethylethyl)-4 hydroxybenzene propanoic acid, 2,2 bis((3-(3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropoxy)methyl) 1,3-propanediyl ester

CAS No.: 6683-19-8

Empirical formula: $C_{73}H_{108}O_{12}$

Molecular weight: 1322

Maximum percentage: 0.1% (w/w)

Toxic properties: toxicological data are not available from scientific literature. However, given its high molecular weight and low concentration, this impurity is unlikely to pose a significant health hazard.

.

Identity: phosphoric acid, tris(2-ethylhexyl)ester
Synonym: triethylhexyl phosphate
CAS No.: 78-42-2
Maximum percentage: 0.08% (w/w)
Toxic properties: very low acute oral toxicity (rat LD_{50}=37g/kg); moderate skin irritant (rabbit); moderate eye irritant (rabbit)(2)

Identity: antimony oxide
Synonym: antimony trioxide
CAS No.: 1309-64-4
Maximum percentage: 0.06% (w/w)
Toxic properties: low acute oral toxicity (rat LD_{50}=3250mg/kg)(3); caused lung and skin irritation, pneumonitis and pneumoconiosis in animals.(4) National exposure standards(5): TWA : 0.5mg/m^3

.Identity: acetic acid, zinc salt
Synonym: zinc acetate
CAS No.: 557-34-6
Maximum percentage: 0.04% (w/w)
Toxic properties: low acute oral toxicity (rat LD_{50}=2510mg/kg)(2,3)

Residual Monomers:

.Identity: pentanedioic acid, dimethyl ester
CAS No.: 1119-40-0
Maximum residual: <0.5% (w/w)
Toxic properties: C_4-C_6 alkyl dicarboxylic acid esters generally have low acute oral toxicities (rat LD_{50} > 1000mg/kg) but may have slight irritant effects on the eyes and skin. Also given the low vapour pressures, these compounds normally would not constitute a significant health hazard.(6)

Identity: 1,4-benzenedicarboxylic acid, dimethyl ester

- **Synonym:** dimethyl terephthalate
- **CAS No.:** 120-61-6
- **Maximum residual:** <0.5% (w/w)
- **Toxic properties:** low acute oral toxicity (rat LD_{50}=4390mg/kg); moderate eye irritant (rabbit).(2,3)

.Identity: 1,2-propanediol

- **Synonym:** propylene glycol
- **CAS No.:** 57-55-6
- **Maximum residual:** <0.5% (w/w)
- **Toxic properties:** very low acute oral toxicity (rat LD_{50}=20g/kg); mild eye irritant (rabbit) and mild skin irritant (human)(2,3).

.Identity: 1,2,3-propanetriol

- **Synonym:** glycerine; glycerol
- **CAS No.:** 56-81-5
- **Maximum residual:** <0.5% (w/w)
- **Toxic properties:** very low acute oral toxicity (rat LD_{50}=12600mg/kg); mild skin irritant (rabbit); mild eye irritant (rabbit)(2,3)
  National Exposure Standard(5):
  TWA: 10mg/m3 (mist)

Note: these impurities present at an overall concentration of less than 0.3% by weight of the polymer are unlikely to pose a serious health hazard.

6. INDUSTRIAL USES

"Polyester" is intended to be used exclusively as a binder resin in commerical toner and developer formulations (Kodak Coloredge Cyan Toner, Kodak Coloredge Cyan Developer, Kodak Coloredge Yellow Toner, Kodak Coloredge Yellow Developer, Kodak Coloredge Magenta Toner and Kodak Coloredge Magenta Developer). The toner formulations will contain 95-99% by weight of the polymer and the developer formulations will contain only 10-15%. The

formulations will be imported in sealed polyethylene cartridges each containing 350 grams or 850 grams of the products.

Other ingredients of the formulations are magenta rhodamine pigment* (for Magenta Toner and Developer), cyan phthalocyanine pigment* (for Cyan Toner and Developer), yellow azo pigment (for Yellow Toner and Developer), CA-10* (for Toners), CGH polymer* (for Cyan and Yellow Toner) and strontium ferrite (CAS No. 12023-91-5, for Developers).

The estimated quantity of "polyester" to be imported into Australia is less than 500 kilograms per year for the first five years.

*Note: full assessment reports and summary reports for these substances have been published by the Director of Chemicals Notification and Assessment under subsection 38(5) of the Industrial Chemicals (Notification and Assessment) Act 1989.

7. PUBLIC AND OCCUPATIONAL EXPOSURE

The formulations will be imported into Australia in sealed cartridges which are ready to use in photocopiers. Only the 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 polymer matrix. Therefore, it can be expected that there will be very low public and worker exposure to the "polyester" and the formulated products under normal use conditions.

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

8. ENVIRONMENTAL EXPOSURE

8.1 Release

As the formulated toners will only be used for office photocopying, it is expected that only a negligible amount of toner and developer 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(7).)

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(8). It is unclear how much of the polymer will detach from paper as a result of recycling. However, the low volume of chemical that will be imported (<500 kg/yr over the next five years) should result in a negligible amount of polymer being released to the environment through separation from the paper.

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(9).

Given its high molecular weight and polydispersity (maximum percentage of low molecular weight species (molecular weight <

1000) = <0.02%), it is anticipated that "polyester" 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

Tests of oral toxicity, dermal toxicity, skin irritation and eye irritation were not conducted for the "polyester", but for the Kodak Magenta Toner which contained 95-99% by weight of the "polyester", 1-5% magenta rhodamine pigment and less than 2% of CA-10. Given in Table 1 is a summary of the acute toxicity tests conducted for the toner.

Table 1. Summary of acute toxicity of Kodak Magenta Toner (which contained 95-99% by weight of the "polyester", 1-5% magenta rhodamine pigment and less than 2% of CA-10).

Test	Species	Outcome	Ref.
Oral	Rat	LD_{50} > 5000mg/kg (M&F)	(10)
Dermal	Guinea pig	LD_{50} > 2000mg/kg (M&F)	(11)
Skin irritation	Guinea pig	slight irritation	(12)
Eye irritation	Rabbit	slight irritation	(13)

9.2.1 Oral Toxicity

A limit test was carried out in a group of 5 male and 5 female rats using the formulated product. Each of the animals were treated with 5000mg/kg of the Kodak Coloredge Magenta Toner (which contained 95-99% by weight of the "polyester", 1-5% magenta rhodamine pigment and less than 2% of CA-10) by gavage in 0.5% guar gum. None of the animals died within 14 days of the treatment. The only clinical sign observed in the animals was purple diarrhoea four hours after the administration, which subsided after two days. Gross necropsy revealed no macroscopic pathological changes. The oral LD_{50} was greater than 5000mg/kg for the toner(10).

9.2.2 Dermal Toxicity

A limit test was carried out in a group of 5 male and 5 female guinea pigs using the formulated product. A 2000mg/kg dose of the Kodak Coloredge Magenta Toner (which contained 95-99% by weight of the "polyester", 1-5% magenta rhodamine pigment and less than 2% of CA-10), moistened with water, was administered to the skin of each test animal. None of the animals died within 14 days following treatment. The only effect observed was magenta staining of the skin at the site of application. The dermal LD_{50} was greater than 2000mg/kg for this toner(11).

9.2.3 Skin Irritation

Five guinea pigs were used in an acute dermal irritation test. The Kodak Coloredge Magenta Toner, moistened with water, was applied in a single dose of 0.5 gram to the skin of each test animal. The animals were then examined 24, 48 hours and two weeks after patch removal. It was stated that slight irritation and magenta staining of the skin were observed in these animals, but the type of irritation (erythema, oedema, etc) was not defined. Moreover, it is possible that signs of irritation might have been masked by the magenta staining of the skin(12).

9.2.4 Eye Irritation

Eye irritation was measured by instilling 0.1 gram of the Kodak Coloredge Magenta Toner into the conjuntival sac of one eye in each of six New Zealand white rabbits. The other eye remained untreated and served as a control. Three of the animals had their treated eyes washed following instillation. All the eyes were examined for signs of irritation of the conjunctivae, cornea and iris at 1, 24, 48 and 72 hours after the instillation. Slight redness of the conjunctivae was observed in all test animals one hour after the treatment, but had subsided completely at 48 hours. Eye washing did not appear to reduce irritation significantly. No other symptoms were noted(13).

9.3 Overall Assessment of Toxicological Data

Toxicity tests revealed that the Kodak Coloredge Magenta Toner exhibited very low acute oral and dermal toxicities in test animals (oral LD_{50} > 5000mg/kg body weight in rats and dermal LD_{50} > 2000mg/kg body weight in guinea pigs).

The Kodak Coloredge Magenta Toner appeared to be a slight skin and eye irritant. It is anticipated that the toner dust, if inhaled, will also slightly irritate the upper respiratory tract.

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

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, which are the organisms most likely to be exposed.

10.2 Assessment of Environmental Hazard

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 is relatively small (<500 kilograms per year for the first five years). Although its degradation products are not known, the disposal of the polymer is likely to result in a low environmental hazard.

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.

Public and worker exposure to the "polyester" and the formulated toner and developer products is likely to be minimal under normal use conditions. From the very low acute oral and dermal toxicities observed in test animals and the low irritating potential to the skin, eyes and upper respiratory tract, exposure to both the "polyester" and the Magenta 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 "polyester" and the formulated toner and developer products, in general 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 each of the Material Safety Data Sheets of the formulated products should be made available to all personnel who may have exposure to the toner; and

. photocopier 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*(14).

13. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Industrial Chemicals (Notification and Assessment) Act 1989 (the Act), secondary notification of the "polyester" shall be required by Kodak (Australasia) 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) Sax N I & Lewis R J, *Dangerous Properties of Industrial Materials*, 7th edition, Volume 1-3, 1989.

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

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

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

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

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

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

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

(10) Acute Oral Toxicity of Kodak Magenta Toner, Data on File, Eastman Kodak, U.S.A., Report KPD-0153-412(10/85), 1986

(11) Acute Dermal Toxicity of Kodak Magenta Toner, Data on File, Eastman Kodak, U.S.A., Report KPD-0153-412(3/83), 1986

(12) Acute Skin Irritation of Kodak Magenta Toner, Data on File, Eastman Kodak, U.S.A., Report KPD-0153-311(10/85), 1985

(13) Acute Eye Irritation of Kodak Magenta Toner, Data on File, Eastman Kodak, U.S.A., Report TX-87-43, 1987

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