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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

Bis(29H,31H-PHTHALOCYANINATO(2-)-N29, N30, N31, N32-)

(.mu)(1,1,3,3-TETRAPHENYL-1,3-DISILOXANEDIOLATO(2-)

(01:03)) DIALUMINIUM

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT

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(.mu) (1,1,3,3-TETRAPHENYL-1,3-DISILOXANEDIOLATO (2-)

(01:03)) DIALUMINIUM

1. IMPORTER

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

2. IDENTITY OF THE CHEMICAL

Chemical name: Bis(29H, 31H-phthalocyaninato(2-)-N29, N30, N31, N32-) (.mu) (1,1,3,3-tetraphenyl-1,3-disiloxanediolato(2-)(01:03)) dialuminium

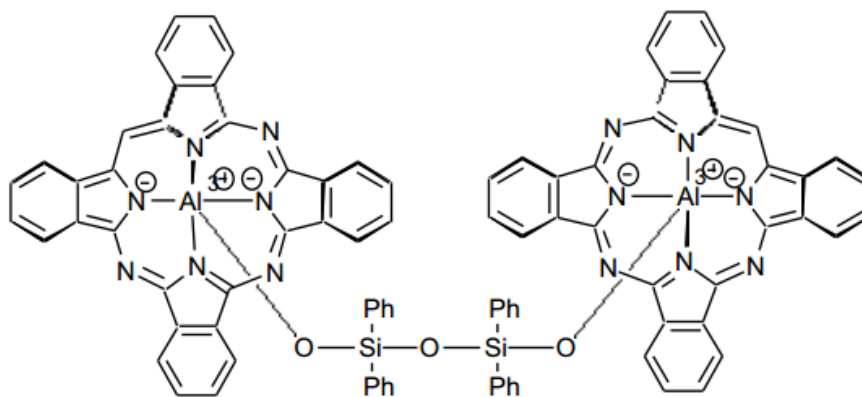
Chemical Abstract
Service (CAS) No.: 81422-13-1

Other name: Bis(phthalocyaninylalumino)tetra-phenyldisiloxane

Trade name: Cyan phthalocyanine pigment

Empirical formula: C₈₈H₅₂Al₂N₁₆O₃Si₂

Structural formula:



Molecular weight: 1491.63

Spectral data: Infrared (IR) spectrum (major absorption bands for identification: 1080 (broad), 1125 (strong), 1325 (strong), 1425 (moderate), 1500 (weak) and 1600 cm⁻¹), Nuclear magnetic resonance (NMR) spectrum and ultraviolet/visible (UV/VIS) absorption spectrum

3. PHYSICAL AND CHEMICAL PROPERTIES

Cyan phthalocyanine pigment is a blue, non-volatile, crystalline powder at room temperature and atmospheric pressure. Its physical and chemical properties include:

Melting point: 225°C (with decomposition)

Stability: will decompose at temperatures above 225°C, emitting carbon dioxide and toxic fumes such as carbon monoxide and oxides of nitrogen.

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

4. METHOD OF DETECTION AND DETERMINATION

The chemical can be separated by high performance liquid chromatography (HPLC) and identified by IR, NMR and UV/VIS spectrophotometry.

5. PURITY OF THE CHEMICAL

Degree of purity: 98% (w/w) (by HPLC)

Toxic or hazardous impurity:

Identity: SP(5-12)-hydroxy(29H, 31H-phthalocyanato(2-) N29, N30, N31, N32)-aluminium
 CAS No.: 15554-15-1
 Maximum percentage: 2% (w/w)

6. INDUSTRIAL USES

Cyan phthalocyanate pigment is intended to be used exclusively as a cyan colouring agent in commercial toner and developer formulations (Kodak Coloredge Cyan Toner and Kodak Coloredge Cyan Developer). The toner and developer formulations will contain <5% by weight of the pigment.

Other ingredients of the formulations are polyester (CAS No: 120611-31-6)*, CGH polymer* (for toner only), CA-10* (for toner only) and strontium ferrite (CAS No. 12023-91-5, for Developer only).

The estimated quantity of cyan phthalocyanine pigment to be imported into Australia is less than 50 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 cyan phthalocyanine pigment 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 pigment is fixed will ultimately be incinerated, disposed of in a landfill, or recycled. When incinerated, the pigment will be degraded. When disposed in a landfill, because the pigment will remain encapsulated in the water insoluble polymer matrix which is fused to the paper, the pigment should not readily degrade and, therefore, is likely to persist.

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(1). It is likely that after the paper recycling processes, the pigment may be discharged in the aqueous water stream from recycling plants.

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Acute Toxicity

Table 1. Summary of acute toxicity studies with cyan phthalocyanine

Test	Species	Outcome	Ref.
Oral	Rat	LD50 > 5000mg/kg (M&F)	(2)
Dermal	Rat	LD50 > 2000mg/kg (M&F)	(3)
Skin irritation	Rabbit	non irritant	(4)
Eye irritation	Rabbit	moderate irritant	(5)
Skin sensitisation	Guinea pig	non-sensitising	(6)

9.1.1 Oral Toxicity

A limit test was carried out in a group of 5 male and 5 female CD(SD)BR rats. Each of the animals was treated with 5000mg/kg of cyan phthalocyanine pigment in corn oil by gavage in a single dose. None of the animals died within 14 days of the treatment. The only sign observed in the animals was blue discoloration of the faeces, which occurred from Day 1 through 2 after administration. The discoloration subsided after two days. Gross necropsy revealed no macroscopic pathological changes. The oral LD50 was greater than 5000mg/kg for the pigment. (2)

9.1.2 Dermal Toxicity

A limit test was carried out in a group of 5 male and 5 female CD(SD)BR rats. A 2000mg/kg dose of cyan phthalocyanine pigment, moistened with water, was applied to the clipped back of each animal and was held in place under an occlusive wrap for 24 hours. At the end of the exposure period, the residual chemical was washed away with running water. None of the animals died within 14 days of the treatment. The only adverse effect observed in most of these animals was blue discoloration of the hair at the site of application. Gross necropsy revealed no macroscopic pathological changes. The dermal LD50 was greater than 2000mg/kg for the pigment. (3)

9.1.3 Skin Irritation

Three New Zealand White rabbits were used in an acute dermal irritation test. Cyan phthalocyanine pigment, moistened with water, was applied in a single dose of 0.5 gram to the clipped dorsal skin of each test animal under an occlusive wrap for four hours. At the end of the exposure period, residual chemical was washed away with running water. The animals were then examined for signs of erythema, oedema, necrosis and eschar formation at 1, 24, 48 and 72 hours, and 7 and 14 days after patch removal. No sign of irritation was observed at the periphery of the site of application, where the skin was unstained. (4)

9.1.4 Eye Irritation

Eye irritation was measured by instilling 0.1 gram of cyan phthalocyanine pigment into the conjunctival sac of one eye in each of six New Zealand white rabbits. The other eye of each rabbit remained untreated and served as a control. Three of the animals had their treated eyes washed following instillation. All treated eyes were examined for signs of irritation of the conjunctivae, cornea and iris at 1, 24, 48 and 72 hours and 7 days after the instillation. Slight redness of the conjunctivae was observed in all test animals one hour after the treatment. In all washed eyes, the slight redness subsided completely at 72 hours. In the three unwashed eyes, irritation progressed to moderate and strong erythema of the conjunctivae in 2 animals, and to mild corneal opacity in 1 animal, which recovered completely at 72 hours. These results indicate that cyan phthalocyanine pigment is a moderate eye irritant in rabbits and immediate eye washing appeared to reduce irritation significantly. (5)

9.1.5 Skin Sensitisation

Prior to the induction and sensitisation test, the maximum non-irritant dose was determined in a separate pilot irritation study. In this pilot study, solid cyan phthalocyanine pigment, moistened with water to give a

100% solution, was administered in a single dose of 0.5 gram to the clipped dorsal skin of each of 3 (HA)BR Hartley guinea pigs under an occlusive wrap for six hours. At the end of the exposure period, the residual chemical was wiped off. The animals were then examined for signs of erythema and oedema at 24 and 48 hours after the application. No sign of irritation was observed at this dosage.

A Buehler test was carried out in a test group and a control group of 10 (HA)BR Hartley guinea pigs each. In this induction and challenge study, the same dose and application procedures were used and repeated weekly for three weeks in the 10 test animals. Two weeks after the last induction exposure, a single dose of the test chemical was applied to each of the 10 test and 10 control animals in the same application procedures but at different sites on the back of the animals. The animals were examined for signs of erythema and oedema at 24 and 48 hours after the challenge application. No sign of irritation was observed in any of the irritation control or induction and challenge groups of animals. These results indicate that cyan phthalocyanine is a non-sensitiser in guinea pigs.(6)

9.2 Mutagenicity

Cyan phthalocyanine pigment was tested for mutagenicity in the Ames Salmonella/Microsome Reverse Mutation Assay using Salmonella typhimurium strains TA1535, TA1537, TA1538, TA98 and TA100, both in the presence and absence of an exogenous mammalian metabolic activation system (Aroclor induced S-9). The dose levels used in the test ranged from 50 - 10000 ug per plate and the mutation assays were conducted using 3 plates at each dose level. Tests were performed twice.

An increase in the number of revertant colonies per plate was not observed in any of the five strains, both in the presence and absence of an exogenous mammalian activation system. These results indicate that under the test conditions, cyan phthalocyanine pigment was not genotoxic in Salmonella typhimurium. (7)

9.3 Overall Assessment of Toxicological Data

Cyan phthalocyanine pigment exhibited very low acute oral and dermal toxicities in test animals (oral LD50 > 5000mg/kg and dermal LD50 > 2000mg/kg in rats). The chemical is not irritating to the skin and does not cause sensitisation. However, the test material was a moderate eye irritant. Immediate washing of the eye however reduced the irritant response.

In the Ames test for mutagenicity, cyan phthalocyanine pigment was not genotoxic in Salmonella typhimurium.

10. ASSESSMENT OF ENVIRONMENTAL HAZARD

Environmental exposure to the pigment could occur through two main routes: when paper containing the pigment is recycled; and when such paper is disposed of in a landfill. The quantity of pigment that will be fixed to paper as a result of photocopying is relatively small (<50 kilograms per year for the first five years). Therefore, even though in the paper recycling processes the pigment may be discharged in the aqueous water stream from recycling plant, it is unlikely that toxic concentrations would result, even before dilution of any discharges by

the receiving water. Also given its low environmental exposure through normal use, the pigment should pose a low environmental hazard.

11. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Public and worker exposure to cyan phthalocyanine pigment 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 moderate irritating potential to the eyes, exposure to both the cyan phthalocyanine pigment and the toner and developer 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 cyan phthalocyanine pigment 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(8).

13. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the Industrial Chemicals (Notification and Assessment) Act 1989 (the Act), secondary notification of cyan phthalocyanine pigment 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) Forestry Canada, Industry/Trade and Technology Directorate and Environment Canada, Final Report, Waste Paper Study (to end of 1989), p.56-57
- (2) Acute Oral Toxicity of bis(phthalocyaninylaluminio)-tetraphenyl disiloxane, Data on File, Eastman Kodak Company, U.S.A., Report TX-88-52, 1988

- (3) Acute Dermal Toxicity of bis(phthalocyaninylalumino)-tetraphenyl disiloxane, Data on File, Eastman Kodak Company, U.S.A., Report TX-88-53, 1988
- (4) Acute Skin Irritation of bis(phthalocyaninylalumino)-tetraphenyl disiloxane, Data on File, Eastman Kodak Company, U.S.A., Report TX-87-213, 1987
- (5) Acute Eye Irritation of bis(phthalocyaninylalumino)-tetraphenyl disiloxane, Data on File, Eastman Kodak Company, U.S.A., Report TX-87-212, 1987
- (6) Skin Sensitisation Study (Buehler method) of bis(phthalocyaninylalumino)tetraphenyl disiloxane, Eastman Kodak Company, U.S.A., Report TX-89-44, 1989
- (7) Mutagenicity Test on Cyan phthalocyanine pigment in the Ames Salmonella/microsome reverse mutation assay, Data on File, Eastman Kodak Company, U.S.A., Report 10692-0-401, 1989
- (8) National Occupational Health and Safety Commission, Office Copying Machines, AGPS, Canberra, December, 1989