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NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME

FULL PUBLIC REPORT

CALCIUM BOROSILICATE

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For Enquiries please contact Ms Karen Bell at:

 $Street\ Address:$ 92 Parramatta Rd Camperdown, NSW 2050, AUSTRALIA

Postal Address: GPO Box 58, Sydney 2001, AUSTRALIA Telephone: (61) (02) 565-9466 FAX (61) (02) 565-9465

Director

Chemicals Notification and Assessment

FULL PUBLIC REPORT

CALCIUM BOROSILICATE

1. <u>IMPORTER</u>

Hodgsons Dye Agencies Pty. Ltd., 56-58 Bay Street, Broadway, SYDNEY NSW 2007

2. <u>IDENTITY OF THE CHEMICAL</u>

Chemical name: calcium borate silicate

(CAS Index Name)

Chemical Abstracts Service

(CAS) Registry No.: 59794-15-9

Other name(s): calcium borosilicate (used

throughout this report) calcium boronsilicate calcium silico

borate

Trade name(s): Halox CW-230, CW-291, CW-221,

CW-22

Molecular formula: 1.4 Ca0.0.5 B203.Si02.H20

Structural formula: Not Applicable

Molecular weight: 180.1

Method of detection and determination:

Chemical analysis, Xray diffraction, element content by spectrographic means.

Spectral data: IR spectrum; maximum absorbance at 3440,

1640, 1410, 1190-900 cm^{-1} .

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa: White, fine powder

Odour: Odourless

Melting Point: >1540 °C

Specific Gravity: 2.65

Vapour Pressure: Not Applicable

Water Solubility: 0.034q/L

Partition Co-efficient Not applicable, in (n-octanol/water): view of expected

insolubility of this
inorganic substance in

octanol.

Hydrolysis as a function of pH: No information was

provided. As the pigment is manufactured in an aqueous medium at 80°C, hydrolytic stability may

be assumed.

pH:
pH in an aqueous medium

is stated to be 10.1.

Adsorption/Desorption: Not measured. The

pigment may be expected
to be immobile in soils
by comparison with

borosilicate minerals.

Dissociation Constant: Not Determined

Flash Point: Not Applicable

Decomposition Temperature: Decomposes at

temperatures > 1540°C

Explosive Properties: Not Explosive

Reactivity/Stability: Stable

Particle size distribution: Range 3.4-4.2µm

4. PURITY OF THE CHEMICAL

Degree of purity: 100%

Toxic or hazardous impurity/impurities: None

Non-hazardous impurity/impurities: (> 1% by weight) None

Additive(s)/Adjuvant(s): None

5. <u>INDUSTRIAL USE</u>

The notified chemical will be imported into Australia in quantities rising from 10 tonnes in the first year to 100 tonnes after five years. Calcium borosilicate will be used in solvent based and water based paints as an anticorrosive and flame retardant agent. Calcium borosilicate is listed on the United States Inventory under the Toxic Substances Control Act.

6. OCCUPATIONAL EXPOSURE

Occupational exposure may occur during the formulation of paint containing the notified chemical or during application of the paint and clean up after application.

The notified chemical will be transported in paper sacks on shrink wrapped pallets. During manufacture of the paint the bag will be opened and the contents emptied into a mixer, usually a high speed stirrer. It is expected that the paint will be added to a liquid so that dust will be minimised after addition. Local exhaust ventilation is expected to be used to minimise dust during the actual emptying of the bag. Exact conditions of use are not stated as they may vary from site to site.

The finished paint will be applied by brush or by spray in domestic use. For industrial use the paint will be applied in spray booths or by dipcoaters or by electrostatic spray. At this stage the notified chemical will be bound into paint in either the liquid or the dry form and is not expected to be biologically

available. Hazards during application of paint and during wash down procedures are expected to be those normal to painting.

The notifier recommends that any excess of water based paints be allowed to dry in the can before disposal and that solvent based paints be disposed of in accordance with the hazards of the other ingredients.

7. PUBLIC EXPOSURE

Under normal conditions, the potential for public exposure to calcium borosilicate is low. The chemical is manufactured outside Australia and is to be imported in bags on shrink wrapped pallets in quantities up to 100 tonnes p.a. in the next 5 years. It is to be used as a paint pigment for anti-corrosive rust resistant paints. The end products will be used in industrial maintenance and domestic use. The pigment is bound in the paint in liquid form and in the dried film. The chemical contained in any release of the end use coating into the atmosphere would be encapsulated by the binder in the formulation.

Empty bags will be collected and disposed by landfill. Raw chemical waste has been estimated at 0.01% in the manufacturing process and will be disposed via landfill. Waste handling procedures of the end products would be by sealed drums to landfill.

8. ENVIRONMENTAL EXPOSURE

. Release

Formulation, handling and disposal

The pigment is imported on shrink wrapped pallets in individual paper bags, which will be split and emptied into a mill or a high speed mixer for incorporation into solvent/alkyd based paint formulations. Formulation will take place at 15 sites around Australia. Empty bags will be stacked and formulation wastes packed into sealed drums before consignment to landfill. The notifier indicates that losses during manufacture would be in the order of 0.01%, and dust generated would be contained by dust extractors. The Material Safety Data Sheet recommends that

spillages of the pigment be swept up for landfill or incineration.

- Use

Paints containing calcium borosilicate will be used in industrial and domestic situations. Application will be by spray or brush. In domestic situations, spray application is

likely to lead to paint losses to the atmosphere with subsequent deposition of the paint film containing the pigment to soil, particularly if conducted out of doors. However, such exposure will be widely dispersed. The notifier indicates that paint will be applied in controlled spray booths in industrial situations. Standard pollution control equipment installed at such facilities will collect paint wastes as a sludge for disposal to landfill (1). The notifier is unable to provide detailed estimates of likely releases to the environment during use of the pigment. However, significant exposure is not expected because of the widely dispersed nature of the proposed use in paints.

. Fate

Only the boron in the composite pigment will be considered here since the other constituents (lime, silica and water) are not of any recognised environmental concern. This and the following sections draw heavily from the recently published safety assessment of boron in aquatic and terrestrial environments (2).

A brief outline of the manufacture of calcium borosilicate, which takes place in the USA, may be informative regarding its structure and likely environmental behaviour. According to the patent (3), the composite pigment is prepared from the mineral wollastonite (CaO.SiO₂), which is stirred into water, treated with slaked lime and anhydrous boric acid, and subjected to prolonged attrition in a pebble mill which raises the temperature to around 80°C. The pigment is then filtered, dried and pulverised.

Little appears to be known about the structure of calcium borosilicate, which varies in composition according to the formulae $1.2\text{CaO.}0.2\text{B}_2\text{O}_3.\text{SiO}_2.0.5\text{H}_2\text{O}$ (Halox CW-22, 221 and 291) and $1.4\text{CaO.}0.5\text{B}_2\text{O}_3.\text{SiO}_2.0.5\text{H}_2\text{O}$ (Halox CW-2230). The patent notes that separation of the components of the composite by physical means alone is impossible, and it would appear that the CaO, B_2O_3 and SiO_2 units form a covalently bonded network. Accordingly, the

behaviour of calcium borosilicate in the environment should be similar to that of borosilicate minerals in general.

Boron occurs naturally in the environment as borosilicates in sediment and sedimentary rocks, and is slowly mobilised into soils and the aquatic environment during weathering. Once released from silicate structures, boron forms stable species in solution such as $B(OH)_3$, $B(OH)_4$ - and complex polyanions, which in turn react with clays in depositional waters and are returned to sediment. Release of soluble boron compounds from the composite pigment can be expected to be retarded by its encapsulation in the paint coating, but otherwise it should behave analogously to natural borosilicates in the environment.

Environmental exposure to the pigment appears likely to arise mainly when the paint is applied by spray, which will involve losses to the atmosphere and subsequent deposition to soil if conducted out of doors. However, the notifier indicates that industrial applications will take place in controlled spray booths. Significant environmental contamination from domestic uses appears unlikely.

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Acute Toxicity

Table 1 Summary of the acute toxicity of calcium borosilicate

Test	Species	Outcome	Reference
Oral Dermal Toxicity	Rat Rabbit	LD50>5,000 mg/kg LD50>2,000 mg/kg	(4) (5)
Skin irritation	Rabbit	Slightly irritating	(6)
Eye irritation	Rabbit	moderately irritatin	g (7)

9.1.1 Oral Toxicity (4)

A group of 5 male and 5 female Sprague Dawley ${\rm CD^R}$ albino rats received single doses of 5000 mg/kg calcium borosilicate. The chemical was administered by oral intubation as a 30% suspension in 1% carboxymethylcellulose. Animals were observed for a 14 day period before termination of the study. No control group was included.

No deaths were observed during the study. Clinical signs and symptoms were minimal. One female rat showed slight weight loss at day 14. One male had a soft stool at 2 hours after dosing. At necropsy abnormalities noted were lung alterations considered similar to control animals sacrificed in a similar manner (CO_2 inhalation).

The oral LD50 of calcium borosilicate was found to be > 5,000mg/kg in this test.

9.1.2 Dermal Toxicity (5)

The dorsal skin representing 20% of the total body surface was clipped on 10 New Zealand White rabbits, 5 male and 5 female. Eighteen hours later an amount corresponding to 2,000 mg/kg calcium borosilicate was applied to the skin surface, moistened with distilled water and covered with an occlusive bandage. In 5 of the 10 animals the clipped skin site was abraded immediately prior to application of the test material. Twenty four hours after application, the occluded bandage was removed and the test site wiped free of excess test material. Animals were observed 1, 2 and 4 hours and then daily after administration of the test substance to the skin.

No deaths occurred during the study period. Barely perceptible erythema was observed in 2 of the 5 animals in which the compound had been applied to abraded skin and 3 out of 5 animals in which the compound had been applied to non-abraded skin. Two animals showed decreased activity and 1 faecal staining of the anogenital area within 24 hours. Some animals showed discharges from the nose or eyes in the second week after dosing. Examination at necropsy showed no changes considered related to administration of the test substance. Five of the 10 animals had liver fissures on examination. The pathologist's opinion was that the fissures were due to handling of the liver during the examination. Other changes noted at necropsy were considered common to laboratory animals.

LD50, in this test, was found to be greater than 2,000 mg/kg in rabbits.

9.1.3 Skin Irritation (6)

The potential of calcium borosilicate for skin irritation was determined using the abraded and non-abraded skin of New Zealand White Rabbits. The dorsal skin of 3 male and 3 female rabbits was clipped the day before dosing and the skin on the left side of all animals was abraded immediately prior to administration of 0.5g calcium borosilicate moistened with 0.5ml saline to the abraded and non-abraded skin. Both sites were covered with an occlusive dressing for a 24 hour period. Skin irritation was determined by observation 30 minutes and 48 hours after removal of the dressing (24 hours and 72 hours after application).

There was no significant difference between the response of intact and of abraded skin. At 24 hours after application, all sites showed erythema ranging from very slight to moderate-to-severe. Oedema was present at abraded and non-abraded skin sites in 2 animals, being barely perceptible in one and slight in the second. At 72 hours the irritation was much decreased.

Calcium borosilicate appears to be slightly irritant to the skin.

9.1.4 Eye Irritation (7)

Eye irritation was determined in 9 New Zealand White Rabbits. Calcium borosilicate (59 mg) was instilled into the right eye of the rabbits. In 3 animals, the eye was rinsed 30 seconds later. The left eye remained untreated in all animals and served as a control. Eyes were examined visually at 24, 48, 72 hours and 4 and 7 days after administration. Fluoroscein examination was conducted at 24 hours to assess any corneal injury.

No effect on the iris or the cornea was reported at any observation period in any animal. Redness of the conjunctiva was observed in all 6 unwashed treated eyes. Chemosis (swelling) was observed in two. One animal was reported as having necrosis of conjunctival tissue at 24 and 48 hours. All unwashed eyes were clear at the completion of the study on day 7.

Washing was palliative. Two animals showed minimal conjunctival irritation and the third showed some degree of redness with some necrosis of conjunctival tissue at 24 and 48 hours. All washed eyes were clear at 72 hours.

The test material, calcium borosilicate, was found to be moderately irritating to the eye.

9.2 Genotoxicity

9.2.1 Salmonella typhimurium Reverse Mutation Assay (8)

A sample of labelled calcium borosilicate CW 2230 was tested for potential mutagenicity in a *Salmonella typhimurium* plate incorporation assay conducted in four strains (TA 100, TA 98, TA 1535 and TA 1537) in the presence and absence of a homogenised rat liver metabolising system (S9 mix) according to OECD guidelines (9)

Due to the insoluble nature of the compound, it was not possible to apply the test substance as a solution. Therefore a suspension of the test substance in dimethyl sulphoxide (DMSO) (1 g/mL) was prepared, allowed to stand overnight at 37°C and the supernatant recovered the following morning for testing. A maximum volume of 100 μL , together with four other dilutions in DMSO at half log intervals, was applied to test plates. DMSO served as the negative control and positive controls were:

TA 100 and TA 1535 sodium azide
TA 98 2-nitrofluorene
TA 1537 9-aminoacridine

2-Aminoanthracene, served as positive control in tests incorporating S-9 mix.

There was no evidence of toxicity even at the highest applied test dose. All positive controls, with and without S-9 mix, produced an increase in revertants. The test supernatant did not induce elevated numbers of revertant colonies at any dose in any of the bacterial strains, compared with the negative controls.

9.3 Overall Assessment of Toxicological Data

Calcium borosilicate has low acute oral and dermal toxicity with moderate eye and slight skin irritation. The effects of the powder by inhalation have not been tested. Dust irritation of the mucous membranes could be expected. The sensitizing potential is also not tested.

An <u>in vitro</u> Ames test indicated that the compound is non-mutagenic. Tests for induction of germ cell damage or mammalian chromosome damage have not been presented. The effects upon skin sensitization, acute inhalation and repeated exposure are unknown. The particles are of a respirable size.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

Borosilicate minerals may be regarded as essentially inert as far as the metabolism of living organisms is concerned (2). No toxic effects from the calcium borosilicate pigment were noted in tests on laboratory rodents.

Boron is an essential nutrient for plant growth, but is also toxic at higher levels. In soils, boron is typically present in silicate minerals and adsorbed onto clays, iron and aluminium hydroxides and organic matter, with only a small fraction in soil solution and available for plant uptake. Boron deficiency has traditionally been the more serious problem, although toxicity symptoms to sensitive citrus crops have been observed in Sicilian orange groves irrigated with untreated sewage containing 2 ppm boron (2).

Specific aquatic toxicological data for the pigment are not available, but recent assessments indicate that boron, the only constituent of the pigment which may exert toxic effects, is not a concern for surface waters at current usage levels. Early life stages of rainbow trout appear to be most sensitive to boron with a recorded LOEC (lowest observed ecotoxic concentration) well below 1 ppm for boric acid in reconstituted water, but toxicity is greatly reduced in natural waters through changes in speciation. Wild healthy rainbow trout inhabit streams in the southwestern US where boron reaches levels as high as 5-15 ppm because of weathering of boron rich formations and deposits (2).

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

While few data are available for the composite pigment, its environmental hazard would not be expected to exceed that of its boric oxide component, which may be slowly released from protective coatings by weathering. Such processes would not be expected to significantly increase environmental exposure to boron compared with weathering of borosilicate minerals and release from other uses, such as detergents containing sodium perborate.

Disposal of paint wastes to landfill is similarly not expected to significantly increase environmental exposure to boron in view of the pigment's mineral character. Release of soluble boron species from the pigment is expected to occur slowly in landfill, if at all, and boron concentrations in landfill leachate will

therefore be low. The predicted environmental hazard of the pigment is minimal.

12..ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

The potential for public exposure to calcium borosilicate is expected to be low in normal circumstances due to its manner of use and disposal. The pigment remains bound in the end product. In the case of an accidental spill, care should be taken with its disposal due to the potential for eye and skin irritation.

The most significant exposure to the notified chemical under normal circumstances is expected to occur during emptying of the bags of chemical and mixing with the other ingredients into a paint. The particle size range of 3.4 to 4.2 micrometers indicates that a significant proportion of the dust will be respirable and the precautions should be taken both to minimise dust and minimise exposure.

Once incorporated into paints, calcium borosilicate is not available and products containing the notified chemical should be used in accordance with the specific hazards of the products.

13. RECOMMENDATIONS

During handling of calcium borosilicate and products containing it the following precautions should be observed:

- . When calcium borosilicate is being added to a paint mixture all precautions should be taken to minimise dusts. Local exhaust ventilation should be used to extract dust particles at the point of mixing.
- . Workers who may be exposed to dusts of the notified chemical either during mixing of paints or during clean up of spills should wear a disposable dust mask conforming with Australian Standard (AS) 1715-1991 (10) full body covering conforming with AS 3765.1-1990 (11) gloves conforming with Australian Standard 2161-1978 (12) safety goggles conforming with Australian Standard 1337-1984 (13).

- Exposure standards (14) for respirable dusts and nuisance dusts should be observed. If the exposure standard for dust is exceeded respirators conforming with Australian Standard 1715-1991 should be worn.
- . Spray painting with paints containing calcium borosilicate when carried out on an industrial scale should utilise appropriately ventilated systems which minimise exposure to sprays and aerosols. In paints applied in domestic use either by spray or by brush appropriate precautions should be observed.
- . Workers using calcium borosilicate and products containing it should have ready access to material safety data sheets.

14. MATERIAL SAFETY DATA SHEET

The Material Safety Data Sheet (MSDS) for calcium borosilicate (Attachment 1) was provided in Worksafe Australia format (15). This MSDS was provided by Hodgson Dye Agencies Pty. Ltd. as part of their notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of Hodgson Dye Agencies Pty. Ltd.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals* (Notification and Assessment) Act 1989 (the Act), secondary notification of calcium borosilicate 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

- (1) P M Randell, Journal of Hazardous Materials, 1992, 29, 275-295.
- L Butterwick, N de Oude and K Raymond, Ecotoxicology and Environmental Safety, 1989, 17, 339-371.
- (3) Hammond Lead Products Inc, Indiana, US Patent No 3,846,148 Novel Composite Pigments, November 5 1974.

- (4) Acute Oral Toxicity Study in Rats. Test material calcium borosilicate: Project No. 6425-80.

 Bio/dynamics Inc. Data on file Halox Pigments
 Pittsburgh, PA, U.S.A
- (5) Acute Dermal Toxicity study in Rabbits. Test material calcium borosilicate. Project No. 6426-80. Bio/dynamics Inc. Data on file, Halox Pigments, Pittsburgh, PA, U.S.A.
- (6) Primary Dermal Irritation Study In Rabbits. Test material calcium borosilicate. Project No. 6427-80.
 Bio/dynamics Inc. Data on file, Halox Pigments,
 Pittsburgh, PA, U.S.A.
- (7) Eye Irritation Study in Rabbits. Test material calcium borosilicate. Project 6428-80. Bio/dynamics Inc. Data on file, Halox Pigments, Pittsburgh, PA, U.S.A.
- (8) Genetic Toxicology Report: Bacterial mutagenicity test, of sample labelled calcium borosilicate (CW 2230) employing a standard (Ames) salmonella plate incorporation, as conducted according to OECD Guidelines for Testing of Chemicals. Data on file, Hodgson's Dye Agencies Pty Ltd, P.O Box 270 Broadway NSW 2007
- (9) OECD Guidelines for the Testing of Chemicals. #
 471 Genetic Toxicology Salmonella typhimurium Reverse
 Mutation Assay
- (10) Australian Standard 1715- 1991 Selection, use and maintenance of Respiratory Protective Devices, Standards Association of Australia Publ, Sydney 1991.
- (11) Australian Standard 3765.1-1990 Clothing for Protection against Hazardous Chemicals Part 1 Protection against General or Specific Chemicals Standards Association of Australia Publ, Sydney 1990.
- (12) Australian Standard 2161-1978 Industrial Safety Gloves and Mittens (excluding Electrical and Medical

Gloves), Standards Association of Australia Publ, Sydney 1978.

- (13) Australian Standard 1337-1984 Eye Protectors for Industrial Applications, Standards Association of Australia Publ, Sydney 1984.
- (14) Exposure Standards for Atmospheric Contaminants in the Occupational Environment. Guidance Note [NOHSC: 3008 (1991)]; National Exposure Standards [NOHSC: 1003 (1991)], 3rd Edition, October 1991.
- (15) Guidance Note for Completion of a Material Safety Data Sheet. [NOHSC: 3001 (1991)], 3rd Edition, October 1991.