Scientific Literature Review

Borosilicate Glasses as Used in Cosmetics

November 29, 2011

All interested persons are provided 60 days from the above date to comment on this Scientific Literature Review and to identify additional published data that should be included or provide unpublished data which can be made public and included. Information may be submitted without identifying the source or the trade name of the cosmetic product containing the ingredient. All unpublished data submitted to CIR will be discussed in open meetings, will be available at the CIR office for review by any interested party and may be cited in a peer-reviewed scientific journal. Please submit data, comments, or requests to the CIR Director, Dr. F. Alan Andersen.

The 2011 Cosmetic Ingredient Review Expert Panel members are: Chair, Wilma F. Bergfeld, M.D., F.A.C.P.; Donald V. Belsito, M.D.; Ronald A Hill, Ph.D.; Curtis D. Klaassen, Ph.D.; Daniel C. Liebler, Ph.D.; James G. Marks, Jr., M.D.; Ronald C. Shank, Ph.D.; Thomas J. Slaga, Ph.D.; and Paul W. Snyder, D.V.M., Ph.D. The CIR Director is F. Alan Andersen, Ph.D. This report was prepared by Lillian C. Becker, Scientific Analyst/Writer.

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INTRODUCTION

This is a review of the available scientific literature relevant to assessing the safety of the borosilicate glasses, calcium sodium borosilicate, calcium aluminum borosilicate, calcium titanium borosilicate, silver borosilicate, and zinc borosilicate, as used in cosmetics. These ingredients function mostly as bulking agents.

The Cosmetic Ingredient Review (CIR) Expert Panel has reviewed the related ingredients silica, alumina magnesium metasilicate, aluminum calcium sodium silicate, aluminum iron silicates, hydrated silica, and sodium potassium aluminum silicate.[1] These ingredients were determined to be safe in the present practices of use and concentration.

Data on calcium borosilicate, which is not an ingredient in the *International Cosmetic Ingredient Dictionary and Handbook*[2], are included since there was little toxicity data found on the ingredients covered in this report.

CHEMISTRY

Definition

The CAS numbers, definitions, and functions for the 5 ingredients in this literature review are provided in Table 1.

It is not currently possible to provide the exact structure of borosilicate glasses. The 2 schools of thought are the random-network hypothesis and the crystallite hypothesis. In the random-network hypothesis, it is thought that the SiO_4 tetrahedra in vitreous silica are bonded irregularly to each other. In the crystallite hypothesis, it is thought that vitreous silica submicroscopically small crystalline areas with an ordered structure are present, but are connected to each other by areas with a disordered structure. Neither of these hypotheses has full support. It is usually assumed that there is a certain short-range order in glass, somewhat similar to the order observed in crystals, but there is a definite absence of long-range order.[3]

Physical and Chemical Properties

Physical and chemical properties are provided in Table 2.

STRUCTURE AND PHYSICAL PROPERTIES

The chemical composition of calcium sodium borosilicate is: SiO_2, 52%; Na_2O, 0.3%; CaO, 22.5%; MgO, 1.2%; Al_2O_3, 14.5%; Fe_2O_3, 0.2%; K_2O, 0.2%, and B_2O, 8.6%.[4]

The borosilicate in a cosmetic was described in a patent document as comprising a cosmetic grade flaky glass constituted of components comprising, by weight, at least 52% alkali metal oxide.[5] The flaky glass may be unmodified, surface coated (silicone), or complexed (titania and rare metal, ultra-marine, or other pigments).

The coordination of the boron network cations readily varies from 3 to 4 depending on composition and temperature, varying the properties.[3] There are large differences caused by varying the size and charge of the "network modifier" cations (e.g. Na^+ vs. Ca^{2+}), B/Si ratio, and Al content.

Borosilicates generally have a lower thermal expansion than soda-lime silica glasses, have good chemical resistance, high dielectric strength and a higher softening temperature than soda-lime silica glasses.[3] Chemical analyses of samples of borosilicates of different compositions showed that B_2O_3 evaporation was practically negligible.

PARTICLE SIZE

In a product designed for cosmetic formulations, the geometric particle size of calcium sodium borosilicate is reported to be 9 – 13 µm.[6] The size distribution is 3 – 6 µm 10%; 8 – 12 µm, 50%; and 16 – 23 µm, 90%.

In cosmetic applications, calcium aluminum borosilicate is used as a substrate for metal oxide colors.[7] When coated with the colors, the particle size is reported to be 20 – 200 µm.

The borosilicate in a cosmetic was reported to have an average particle diameter of 1-100 µm, and an aspect ratio (average thickness dividing the average particle diameter) of ≥ 10.[5]

CALCIUM BOROSILICATE

Calcium borosilicate was reported to be a fine, white, odorless powder with a particle size range of 3.4 – 4.2 µm.[8] The melting point is >1540ºC, specific gravity is 2.65, and it has a water solubility of 0.035 g/L. It is reported to be stable and 100% pure. It is not known if this applies to cosmetic grade calcium borosilicate.

Method of Manufacture

Borosilicate glasses may be prepared by the wet-chemical method.[3] Reagent-grade metal salts (except for sodium and calcium) were introduced as nitrates, boron as boric acid and silicon as a colloidal solution of SiO_2.

The preparation of borosilicate glasses may also be by the sol-gel method, which results in reproducible properties.[3] In this method HBO_3 is dissolved in the colloidal SiO_2 sol; if necessary the sol was heated or diluted. A second solution of all the other glass constituents, as nitrates, was then added. After evaporation of a part of the water or adding ammonia the sol sets to a gel, the gel was dried at 200°C for 16 h, which usually resulted in a friable product that was ball milled for about 1 h. This results in a fine powder in which all dements are intimately mixed. This powder is melted in a Pt-Rh crucible in an electric furnace to a bubble-free glass in 2 h at temperatures varying from 800 to 1400°C (depending on the composition of the glass).

Calcium aluminum borosilicate was manufactured by placing finely divided sodium tetrahydrate pentahydrate (80 g), quartz (100 g), kaolin (180g) and wollastonite (40g) as a dry mix into a small mixer and stirred at low speed.[9] Water was added slowly through a syringe until the mixture formed a crumb. The crumb was heated at 1000°C until it was completely

dry. The dried product was transferred to a fireclay crucible and placed in an electric muffle furnace. The furnace was heated at a rate of 100°C/minute up to a maximum of 150°C where the temperature was held for 90 min. The furnace was then switched off and the crucible was allowed to cool to ambient temperature in the furnace. The product was removed, wrapped in a plastic film and broken up with a hammer. The resulting composition was opaque with a creamy-white color and in particulate form.

The use of high pressure caused an increase of the fraction of tetrahedral boron and the mixing of the boron and silicate structural unit.[10]

Silver borosilicate was prepared through introduction of Ag_2O during the melting process.[11]

It is not known if these methods apply to cosmetic grade borosilicates.

Impurities

Heavy metal impurities of calcium sodium borosilicate are reported to be lead (<10ppm), arsenic (<2 ppm), and mercury (<1 ppm).[6]

Calcium aluminum borosilicate has no free SiO_2; all components are amorphous/non-crystalline.[4]

USE

Cosmetic

Data on ingredient usage are provided to the Food and Drug Administration (FDA) Voluntary Cosmetic Registration Program (VCRP).[12] Calcium sodium borosilicate was used in 681 cosmetic products (673 leave-on products, 365 lipsticks; 8 rinse-off products). Calcium aluminum borosilicate was used in 555 cosmetic products (531 leave-on produces, 283 lipsticks; 23 rinse-off products; 1 diluted for bath product). There were no reported uses for calcium titanium borosilicate, silver borosilicate, or zinc borosilicate. The Personal Care Products Council (Council) is conducting a survey of use concentrations for ingredients in this group.

Non-Cosmetic

Borosilicates are used for laboratory glassware, household cooking ware, industrial piping, bulbs for hot lamps and electronic tubes of high wattage such as X-ray tubes.[3] Multi-component borosilicate glasses have many applications, such as fiber reinforcements in composites, in flat-panel display screens for computers and cell phones, and in nuclear waste sequestration.[13]

TOXICOKINETICS

Absorption, Distribution, Metabolism, and Excretion

There were no toxicokinetic data discovered for the cosmetic ingredients in this report.

TOXICOLOGICAL STUDIES

There were no acute or multiple dose toxicity data discovered for the cosmetic ingredients in this report. Calcium borosilicate, a related chemical, has a dermal LD_{50} > 2000 mg/kg for rabbits and an oral LD_{50} > 5000 mg/kg for rats.

Acute Toxicity

Dermal – Non-Human

CALCIUM BOROSILICATE

The dermal LD_{50} of calcium borosilicate (moistened and applied to ~20% of the body under occlusion; clipped and intact or abraded skin) was reported to be > 2000 mg/kg for New Zealand White rabbits (n = 5/sex).[8,14] There were no deaths. Two animals showed decreased activity and 1 fecal staining of the anogenital area within 24 h. Some animals showed discharges from the nose or eyes in the second week after dosing. Examination at necropsy showed no changes considered related to the test substance.

Oral – Non-Human

CALCIUM BOROSILICATE

The oral LD_{50} of calcium borosilicate (applied as a 30% solution in 1% carboxymethylcellulose) was reported to be > 5000 mg/kg for Sprague Dawley CD^R rats (n = 5/sex).[8,15] One female rat showed slight weight loss at day 14 and 1 male had a soft stool 2 h after dosing.

REPRODUCTIVE AND DEVELOPMENTAL TOXICITY

There were no reproductive or developmental toxicity studies discovered.

GENOTOXICITY

There were no genotoxicity studies discovered. Calcium borosilicate, a related chemical, was not genotoxic in an Ames test.

In Vitro

CALCIUM BOROSILICATE

In an Ames test using *Salmonella typhimurium* (TA100, TA98, TA1535 and TA1537) or borosilicate was conducted. The borosilicate (1 g/mL) was steeped in dimethyl sulphoxide over night and the supernatant was used for the assay. The supernatant, up to 100 µL, was not mutagenic with or without metabolic activation. Controls were sodium azide, 2-nitrofluorene, and 9-aminoaridine and the expected results.[8,16]

CARCINOGENICITY

There were no carcinogenicity studies discovered.

IRRITATION AND SENSITIZATION

There were no dermal irritation or sensitization studies discovered for the ingredients in this safety assessment. Calcium borosilicate was a slight to mild dermal irritant and a moderate ocular irritant to rabbits.

Irritation

Dermal – Non-Human

CALCIUM BOROSILICATE

Calcium borosilicate was moistened and applied to ~20% of the body under occlusion to clipped skin (intact or abraded) of New Zealand White rabbits (n = 5/sex).[17] Mild erythema was observed in 2/5 animals in which the test material was applied to abraded skin and 3/5 animals in which it was applied to non-abraded skin.

Calcium borosilicate (0.5 g in 0.5 ml saline) was administered to the abraded and non-abraded skin of New Zealand White Rabbits (n = 3/sex) under occlusion for 24 h.[8,14] At 30 min and 48 h after removal, there was no difference between the response of intact and abraded skin. At removal, all treatment sites showed erythema ranging from very slight to moderate-to-severe. Edema was present at abraded and non-abraded sites in 2 animals, being barely perceptible in one and slight in the other. At 72 h, the irritation was much decreased. Calcium borosilicate was reported to be slightly irritating to rabbit skin.

Inhalation

A material safety data sheet has the dust exposure guideline of a maximum of 5 mg/m^3.[4]

Ocular

CALCIUM ALUMINUM BOROSILICATE

A material safety data sheet reports that eyes and throat may become irritated if exposed to high concentrations of calcium aluminum borosilicate.[4]

CALCIUM BOROSILICATE

Calcium borosilicate (59 mg) was administered to the right eyes of New Zealand White rabbits (n = 9). The eyes were rinsed after 30 sec in 3 of the rabbits. Eyes were examined at 24, 48, 72 h and at 4 and 7 days. There were no effects on the iris or the cornea observed. Redness of the conjunctiva was observed in all 6 unwashed treated eyes; chemosis was observed in 2. One rabbit was reported to have necrosis of conjunctival tissue at 24 and 48 h. All unwashed eyes were clear on day 7. In the washed group, 2 rabbits showed minimal conjunctival irritation and the third showed some degree of redness with some necrosis of conjunctival tissue at 24 and 48 h. All washed eyes were clear at 72 hours. The authors concluded that calcium borosilicate was moderately irritating to rabbit eyes.[8,18]

SUMMARY

Borosilicate glasses, calcium sodium borosilicate, calcium aluminum borosilicate, calcium titanium borosilicate, silver borosilicate, and zinc borosilicate, are ingredients used in cosmetics. These ingredients function mostly as bulking agents.

Heavy metal impurities of calcium sodium borosilicate are reported to be lead, arsenic, and mercury. Calcium aluminum borosilicate has no free SiO_2; all components are amorphous/non-crystalline.

Calcium sodium borosilicate was used in 681 cosmetic products (673 leave-on products, 365 lipsticks; 8 rinse-off products). Calcium aluminum borosilicate is used in 555 cosmetic products (531 leave-on produces, 283 lipsticks; 23 rinse-off products; 1 diluted for bath product). There were no reported uses for calcium titanium borosilicate, silver borosilicate, or zinc borosilicate. A survey of current use concentrations is underway.

There were no toxicokinetic data discovered for the cosmetic ingredients in this report.

There were no acute or multiple dose toxicity data discovered for the cosmetic ingredients in this report. Calcium borosilicate, a related chemical, has a dermal LD_{50} of > 2000 mg/kg for rabbits and an oral LD_{50} of > 5000 mg/kg for rats.

There were no reproductive or developmental toxicity studies discovered.

There were no genotoxicity studies discovered. Calcium borosilicate, a related chemical, was not genotoxic in an Ames test.

There were no carcinogenicity studies discovered.

There were no dermal irritation or sensitization studies discovered for the ingredients in this safety assessment. Calcium borosilicate was a slight to mild dermal irritant and a moderate ocular irritant to rabbits.

DATA NEEDS

Cosmetic Ingredient Review requests that interested parties submit any available data on calcium sodium borosilicate, calcium aluminum borosilicate, calcium titanium borosilicate, silver borosilicate, and zinc borosilicate. In particular toxicokinetics data, results of toxicology studies, (including genotoxicity), and dermal irritation and sensitization data are needed. In addition, aerodynamic diameter distributions of these ingredients as used in cosmetic products that may be aerosolized are needed to complete this report.

TABLES AND FIGURES

Table 1. Definitions and functions of borosilicate ingredients.[2]

Ingredient CAS No.	Definition	Function
Calcium Sodium Borosilicate 65997-17-3 (generic to all silicate glasses) [1204320-21-7] [308066-97-9]	Calcium Sodium Borosilicate is a glass consisting essentially of calcium and sodium borosilicates. [Essentially, Calcium Sodium Borosilicate is a synthetic product formed by the fusion of boron oxide, silica, sodium oxide, and calcium oxide, or combined sources thereof.]	Bulking agent
Calcium Aluminum Borosilicate 94891-31-3 65997-17-3 (generic to all silicate glasses) [155775-82-9]	Calcium Aluminum Borosilicate is a glass consisting essentially of calcium and aluminum borosilicates. [Essentially, Calcium Aluminum Borosilicate is a synthetic product formed by the fusion of boron oxide, silica, sodium oxide, aluminum oxide, and calcium oxide, or combined sources thereof.]	Bulking agent
Calcium Titanium Borosilicate	Calcium Titanium Borosilicate is a glass consisting essentially of calcium and titanium borosiliates. [Essentially, Calcium Titanium Borosilicate is a synthetic product formed by the fusion of boron oxide, silica, sodium oxide, titanium oxide, and calcium oxide, or combined sources thereof.]	Abrasive, bulking agent
Silver Borosilicate [308062-97-7]	Silver Borosilicate is a synthetic product formed by the fusion of boron oxide, silica, sodium oxide, and silver oxide.	Preservative, skin-conditioning agent-miscellaneous
Zinc Borosilicate 37341-47-2	Zinc Borosilicate is an amorphous glass composition consisting of boron oxide, silicon dioxide, sodium oxide and zinc oxide.	Bulking agent

Table 2. Chemical and physical properties.

Property	Value	Reference
Calcium sodium borosilicate		
Physical Form	Solid Spheres; white powder	[4,6]
Color	White	[6]
Density/Specific Gravity g/cm^3	1.1 0.390	[6,19]
Melting Point ^{o}C	~730	[19]
Water Solubility g/L @ ^{o}C & pH	Insoluble	[19]
Calcium aluminum borosilicate		
Physical Form	Hollow, non-porous spheres	[4]
Color	White	[4]
Odor	None	[4]
Density/Specific Gravity g/cm^2	1.1	[4]
Melting Point ^{o}C	~730	[4]
Calcium titanium borosilicate		
No data found		
Silver borosilicate		
No data found		
Zinc borosilicate		
No data found		

Table 3. Current frequency and concentration of use according to duration and type of exposure.[12] There were no uses reported for calcium titanium borosilicate, silver borosilicate or zinc borosilicate by the VCRP.

	Calcium sodium borosilicate		Calcium aluminum borosilicate	
Use type	**# of Uses**	**Concentration (%)**	**# of Uses**	**Concentration (%)**
Totals/conc. range	**681**		**555**	
Duration of use				
Leave-on	673		531	
Rinse-off	8		23	
Diluted for (bath) use	NR		1	
Exposure Type				
Eye	124		117	
Incidental ingestion	365		283	
Incidental inhalation-sprays	18		14	
Incidental inhalation-powders	27		18	
Dermal contact	252		228	
Deodorant (underarm)	NR		NR	
Hair – non coloring	5		3	
Hair - coloring	NR		NR	
Nail	45		30	
Mucous Membrane	373		305	
Baby products	NR		NR	

NR = not reported; Totals = rinse-off + leave-on product+diluted for bath uses.
[1] In a deodorant and/or a suntan product that may or may not be a spray.
Note: Because each ingredient may be used in cosmetics with multiple exposure types, the sum of all exposure type uses may not equal the sum total uses.

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