Scientific Literature Review

Synthetic Fluorphlogopite as Used in Cosmetics

October 3, 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on this Scientific Literature Review and to identify additional published data that should be included or provide unpublished data which can be made public and included.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 All unpublished data submitted to CIR will be discussed in open meetings, will be available at the CIR office for review by any interested party and may be cited in a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.; Curtis D. Klaassen, Ph.D.; Daniel C. Liebler, Ph.D.; Ronald A Hill, 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.

1101 17th Street, NW, Suite 412 ♢ Washington, DC 20036-4702 ♢ ph 202.331.0651 ♢ fax 202.331.0088 ♢
cirinfo@cir-safety.org

TABLE OF CONTENTS

INTRODUCTION

This is a scientific literature review of the cosmetic ingredient synthetic fluorphlogopite (sometimes spelled fluorophlogopite). Synthetic fluorphlogopite is a synthetic mimic of a mineral that functions in cosmetics as a bulking agent and a viscosity increasing agent – aqueous.

CHEMISTRY

Definition and Structure

Synthetic fluorphlogopite (CAS No. 12003-38-2) is a synthetic mimic of a mica-type, fluorine substituted mineral composed of magnesium aluminum silicate sheets, weakly bound together with potassium (Figure 1).[1]

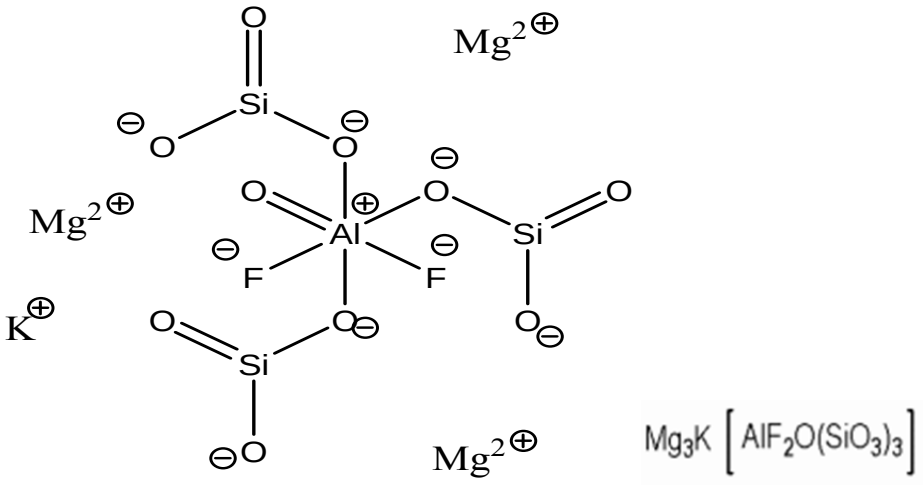

Figure 1. The structure and average formula of synthetic fluorphlogopite.[1]

Phlogopite, the non-florine substituted mineral, like other micas, has a layered structure of magnesium aluminum silicate sheets weakly bonded together by layers of potassium ions.[2] These potassium ion layers produce the perfect cleavage. Single large plates or "books" of phlogopite can grow to considerable size.

Fluorphlogopite differs in that two of the hydroxyl groups, per aluminum atom, are replaced with fluorine atoms. Fluorine is present in the phyllosilicate mineral group in general and in the micas particularly as a substitute for OH. The presence of fluorine enhances the thermal stability of the trioctahedral mica structure.

Physical and Chemical Properties

Physical and chemical properties of synthetic fluorphlogopite are presented in Table 1.

In large pieces, fluorphlogopite is pale yellow and is transparent and non-fluorescent with vitreous to resinous luster; it shows yellowish-white color in thin section.[8] Mohs' hardness is 2–3.

A product description sheet describes synthetic fluorphlogopite as a white to grey free-flowing powder with an average particle size of 10 – 15 μm and a pH range of 5 – 8.[10] The particles have a low degree of surface reactivity (in contrast to natural phlogopites).

Another product data sheet reports that synthetic fluorphlogopite has a pH value of 7.0 - 11.0 (in a 10% Aqueous slurry), a bulk density of 0.240 - 0.300 g/cm^3, and a particle size distribution of 9.0 - 45 micron.[11] Another source reports particles sizes ranging from 20 – 150 μm.[12]

Possible impurities are listed in Table 2. Acid soluble substances are potentially leachable from synthetic fluorphlogopite, including fluorine ions.

Synthetic fluorphlogopite, as opposed to natural fluorphlogopite, is virtually iron free.[8] However, synthetic fluorphlogopite may be intentionally manufactured with iron to more efficiently absorb UV-rays.[13]

Fluorphlogopite has some unique properties due to the replacement of most of the hydroxyl groups on aluminum (that are normally present in non-fluoro phlogopite) with fluoride. However, the aluminum-fluoride bond is only moderately thermodynamically stable. Over time and exposure, atmospheric oxygen and water can replace those fluorides ions, regenerating the more stable hydroxyl groups.

Synthetic fluorphlogopite is stable for 5 years in a sealed container at < 25°C and for at least 1 year once opened.[12] However, fluorine ions (F^-) are reported to leach out of synthetic fluorphlogopite particles and bricks.[15,16]

Method of Manufacture

A reported manufacturing method of synthetic fluorphlogopite designed for industrial-scale batches (up to several tons) involved melting oxide (metal; i.e., aluminum and manganese)-fluoride mixtures at a given "soak" temperature (wherein the contents are liquid; up to 1450°C), and then cooling at a continuous rate of a few degrees per hour between 1400 and 1300°C.[17] This technique produced large fluorphlogopite monocrystals (several centimeters).

Another method synthesized fluorphlogopite single crystals, several millimeters in size, suited to laboratory uses. [18] A mixture of SiO_2, γ-Al_2O_2, MgO, and K_2SiF_6 was first melted at 1450°C for 3 h then cooled to 1385°C at a rate of 100°C/h and then quenched into cold water. The resulting charge was loaded back into the furnace, heated from ~1000°C to 1385°C at a rate of 500°C/h and finally cooled at a rate of 1°C/h down to 1300°C. This procedure led to the formation of large and detachable monocrystals of synthetic fluorphlogopite up to 1 cm in diameter.

The extent of fluorine substitution for OH groups depends on several factors.[8,19] The most important are (1) hydrofluoric acid activity in the fluid during the crystallization and post-crystallization phase; (2) temperature; and (3) cation population of octahedral sheet. Crystal structure may be altered by adjusting the pressure during cooling.[2]

In order to minimize the number of fluoride ions available for leaching, the stoichiometric equivalent of fluorine is decreased to less than one (i.e., less K_2SiF_6 is added) and the melt temperature is decreased (between 900 and 1000ºC).[15] To remove any free fluoride, the resulting ingot is pulverized and the resulting powder is then heat treated at 600 to 1350ºC and then washed with an aqueous solution containing one or more acids or chelating agents.

USE

Cosmetic

Data on ingredients usage are provided to the Food and Drug Administration (FDA) Voluntary Cosmetic Registration Program (VCRP). The VCRP reports that synthetic fluorphlogopite is used in 560 leave-on products and 5 rinse-off products (Table 3).[20] The Personal Care Products Council is currently conducting a survey on the concentrations of use of this ingredient.

Non-Cosmetic

Natural phlogopites are used for their heat and electrical insulating properties.[8]

TOXICOKINETICS

Absorption, Distribution, Metabolism, and Excretion

There were no absorption, distribution, metabolism, or excretion studies of synthetic fluorphlogopite discovered.

TOXICOLOGICAL STUDIES

There were no acute or repeated dose toxicity studies of synthetic fluorphlogopite discovered.

REPRODUCTIVE AND DEVELOPMENTAL TOXICITY

There were no reproductive or developmental toxicity studies of synthetic fluorphlogopite.

GENOTOXICITY

There were no genotoxicity studies of synthetic fluorphlogopite discovered.

CARCINOGENICITY

There were no carcinogenicity studies of synthetic fluorphlogopite discovered.

IRRITATION AND SENSITIZATION

There were no irritation or sensitization studies of synthetic fluorphlogopite discovered.

SUMMARY

Synthetic fluorphlogopite is a synthetic mimic of a natural mica-type mineral that functions in cosmetics as a bulking agent and a viscosity increasing agent – aqueous. Synthetic fluorphlogopite is composed of magnesium aluminum silicate sheets, weakly bound together with potassium.

The VCRP reports that synthetic fluorphlogopite is used in 560 leave-on products and 5 rinse-off products.

DATA NEEDS

Cosmetic Ingredient Review requests that interested parties submit any available data on synthetic fluorphlogopite, particularly the nature of particles of this ingredient, including size, toxicokinetics data, results of toxicology studies, (including genotoxicity), and dermal irritation and sensitization data.

TABLES

Table 1. Chemical and physical properties of synthetic fluorphlogopite.

Property	Value	Reference
Physical Form	Crystaline Fine grained powder	[9,21]
Color	White to grey	[10]
Density/Specific Gravity @ ºC	2.8	[21]
Melting Point ºC	1393-1403	[18]
Water Solubility g/L @ ºC & pH	Insoluble	[12]

Table 2. Possible impurities in synthetic fluophlogopite.

Impurity	Amount	Reference
Acid soluble substances	0.7%	[14]
Lead	< 1.0 ppm	[14]
Arsenic	< 0.5 ppm	[14]
Dissolution amount of (leachable) fluorine	11 ppm	[14]
Iron	0.008 w/w%	[13]
Titanium	0.002%	[13]
Barium	0.001%	[13]
Sodium	0.025%	[13]
Manganese	0.001%	[13]
Chromium	0.002%	[13]
Vanadium	0.001%	[13]
Zinc	0.001%	[13]
Strontium	>0.001%	[13]
Copper	>0.001%	[13]

Table 3. Current frequency of use according to duration and type of exposure provided in 2011. The Personal Care Products Council is currently conducting a survey on the concentrations of use of this ingredient.[20]

	Synthetic fluorphlogopite	
	# of Uses	Concentration (%)
Total/Conc. range	565	
Duration of Use		
Leave-on	560	
Rinse-off	5	
Diluted for (bath) use	NR	
Exposure Type		
Eye	169	
Incidental ingestion	200	
Incidental inhalation-sprays	15	
Incidental inhalation-powders	44	
Dermal contact	336	
Deodorant (underarm)	NR	
Hair – non coloring	2	
Hair - coloring	NR	
Nail	27	
Mucous Membrane	203	
Baby products	NR	

NR = Not Reported; Totals = Rinse-off + Leave-on Product Uses.
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.

REFERENCES

1. Gottschalck TE and Bailey JE eds. International Cosmetic Ingredient Dictionary and Handbook. 13th edition. Washington, D.C.:Personal Care Products Council; 2010.

2. Hazen RM and Finger LW. The crystal structures and compressibilities of layer minerals at high pressure. II. Phlogopite and chlorite. *American Mineralogist*. 1978;63:(3-4):293-296.

3. Boukili, B, Robert, JL, Beny, JM, and Holtz, F. Structural effects of OH —> F substitution in trioctahedral micas of the system: K_2O-FeO-Fe_2O_3-Al_2O_3-SiO_2-H_2O-HF. *Sweizererische Mineralogische und Petrographische Mitteilungen*. 2001;81:(1):55-67.

4. Fetchelkord, M, Behrens, H, Holtz, F, Bretherton, JL, Fyfe, CA, Groat, LA, and Raudsepp, M. Influence of F content on the composition of Al-rich synthetic phlogopite: Part II. Probing the structural arrangement of aluminum in tetrahedral and octahedral layers by ^{27}Al MQMAS and ^{1}H/^{19}F-^{27}Al HETCOR and REDOR experiments. *American Mineralogist*. 2003;88:(7):1046-1054.

5. Mason, RA. Models of order and iron-fluorine avoidance in biotite. *Canadian Mineralogist*. 1992;30:(2):343-354.

6. Munoz, JL. F-OH and Cl-OH exchange in micas with application to hydrothermal deposits. Bailey, SW. Vol. 13. Chantilly, VA: Mineralogical Society of America; 1984:469-493.

7. Papin, A, Sergent, J, and Robert, JL. Intersite OH-F distribution in an Al-rich phlogopite. *Eur.J.Mineral.* 1997;9:(3):501-508.

8. Gianfagna A, Scordari F, Mazziotti-Tagliani S, Ventruti G, and Ottolini L. Fluorophlogopite from Biancavilla (Mt. Etna, Sicily, Italy): Crystal structure and crystal chemistry of a new F-dominant analog of phlogopite. *American Mineralogist*. 2007;92:(10):1601-1609.

9. Redhammer, GJ, Beran, A, Schneider, J, Amthauer, G, and Lottermoser, W. Spectroscopic and structural properties of synthetic micas on the annite-siderophyllite binary: Synthesis, crystal structure refinement, Mössbauer, and infrared spectroscopy. *American Mineralogist*. 2000;85:449-465.

10. Presperse Inc. 2001. Synthecite FNK-100 Synthetic Mica (INCI: Synthetic Fluorophlogopite): Technical Brochure. 4 pages.

11. Sun Chemical. Synmica Super. http://www.specialchem4cosmetics.com/common/cos/services/ingredients/displayproduct.aspx?id=13882. 2011.

12. Sensient Cosmetic Technologies. Material Data Safety Sheet: Covapearl Star Bright 9332 [pamphlet]. South Plainfield, NJ: 2009.

13. Ando A. Application of synthetic mica to cosmetics. *Kobutsugaku Zasshi*. 1995;24:(1):27-29.

14. Topy Industries Ltd. 2011. Test data table (Certificate of Analysis): Synthetic Fluorophlogopite. 1 pages.

15. Ohno K, Kosugi T, Sugimori K, Ando A, Ymamoto M, Suzuki F, Nakamura M, and Tsujita N. Synthetic mica powder manufacturing method thereof and cosmetics having the synthetic mica powder blended therein. 8-20-1990. 570,061:(5,098,712): pp.1-19.

16. Tresvyatskii SG and Vishnevshii VB. New ceamic materials made from synthetic mica. *Sklar a Keramik*. 1970;20:(5):117-119.

17. Hatch, RA, Humphrey, RA, Eitel, W, and Comeforo, JE. Synthetic mica investigations. IX: review of progress from 1947 to 1955. US Department of the Interior, Bureau of Mines Report of Investigations 5337. Cited in: Hammouda T, Pichavant M, Barbey P, and Brearley AJ. Synthesis of fluorphlogopite single crystals. Applications to experimental studies. Eur.J.Mineral. 1995;7(6):1381-1387. 1957.

18. Hammouda T, Pichavant M, Barbey P, and Brearley AJ. Synthesis of fluorphlogopite single crystals. Applications to experimental studies. *Eur.J.Mineral.* 1995;7:(6):1381-1387.

19. Boukili, B, Holtz, F, Bény, JM, and Robert, JL. Fe-F and Al-F avoidance rule in ferrous-aluminous (OH,F) biotites. *Sweizererische Mineralogische und Petrographische Mitteilungen*. 2002;82:549-559.

20. U.S.Food and Drug Administration. FDA database. Cosmetic production fomulation and frequency of use data submitted to the Voluntary Cosmetic Registration Program (VCRP). 2010. Washington, DC: FDA.

21. H.C.Materials Corporation. Synthetic mica products. http://www.hcmat.com/Mica.html. 2011.