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ABSTRACT

This report gives formulations and general procedures for making and applying space environmentally, as well as atmospherically stable black silicate paints. Compositions are given which meet spacecraft self-contamination requirements, have excellent heat resistance, and are strongly semiconductive.

CONTENTS

BLACK SILICATE PAINTS: FORMULATION AND PERFORMANCE DATA ON OSO-H

CHEMISTRY AND PROCESSING TECHNOLOGY FOR BLACK ALKALI-METAL SILICATE PAINTS

Black paint functions, thermodynamically speaking, (1) to provide deep space simulation in the finite confines of the laboratory, and (2) to provide a satellite thermal control surface capable of offering a thermal response time during solar heating intermediate between a white paint and a metallic surface, and a thermal response during cooling in the absence of solar illumination most like that of a white paint. Those black paints receiving by far the most widespread applications are based on the reactivity of the epoxide, isocyanate and carboxyl groups; these functional groups give epoxy, urethane and, for example, polyster, polyimide, polyamide coatings respectively. Less well known are inorganic black paints. The reasons for this are many fold. First, they have only recently been developed, that is, during the latter half of the sixties; second, they do not possess the flexibility of their organic competitors; third, they are more difficult to apply because special precautions must be taken in substrate preparation.

The difficulty in developing an inorganic alkali-metal black silicate resides in the ability of the alkali-metal silicate binder itself to change its chemical composition by spinoidal decomposition, and chemical decomposition upon exposure to carbon dioxide and changes in relative humidity. Spinoidal changes occur because most silicate solutions are metastable and can as a result develop separate chemical phases, eventually arriving at a state of minimum Helmholtz free energy. The duration of the phase separation process may extend over a period of many months, and consequently appears to be diffusion controlled.

Chemical reactions occur because silicates can have pH's up to about 13. At high pH levels, reactions with carbon dioxide become possible yielding bicarbonates, carbonates, and silica as reaction products. Because the products of these processes are colorless and provide scattering surfaces for light, when formed on the surface of the coating, a black paint can acquire a frosty appearance. From a cosmetic viewpoint, this effect is undesirable. On the other hand, optical measurements have demonstrated that the magnitude of the solar absorptance is not significantly effected by the presence of crystallites on the surface of the paint.

The use of sodium silicate as a binder for graphite to make a conductive coating, as well as to increase the photoelectric threshold of a substrate material, is prevalent in the television tube manufacturing industry. For this reason, this type of paint has found use in measuring electric fields in space because it perturbs local fields to a lesser degree than lower threshold materials.

Application of a commercially available formulation of this paint to aluminum spheres flown on SSS for electric field measurements has caused concern because frosting occurred readily under atmospheric conditions. In cooperation with the SSS experimenter,* tests have been performed to study the effect of selected ambients on this coating. Samples of the coating applied to aluminum were placed in desiccators containing nitrogen, carbon dioxide, carbon-dioxide saturated with water vapor, air at 75 and 60 percent relativity humidity.

The sample placed in nitrogen cured satisfactorily. In carbon dioxide, the sample disintegrated completely; so friable was the sample, that optical measurements were not possible. Considering the sodium silicate in this paint to have a commercially available silica to sodium oxide mole ratio of 2, the disintegration can be explained by reacting the excess base,

$$x\ \mathrm{NaOH} + x\ \mathrm{CO_2} \longrightarrow x\ \mathrm{NaHCO_3}, \tag{1}$$

and reacting the remaining sodium salts of silicic acid according to the scheme,

$$\frac{(1-x)}{2}\ \mathrm{Na_2O} \cdot 2\ \mathrm{SiO_2} + y\ \mathrm{CO_2} \longrightarrow$$

$$((1-x) - y - z/2)\ \mathrm{Na_2O} \cdot 2(1 - y - z)\ \mathrm{SiO_2} + y_1\,\mathrm{Na_2CO_3} \tag{2}$$

$$+ 2y_2\,\mathrm{NaHCO_3} + 2z\ \mathrm{Na_2Si_2O_5} + 2y\ \mathrm{SiO_2},$$

where $y = y_1 + 2y_2$. Clearly, if enough SiO_2 is formed, loss of coating integrity is inevitable; formation is assisted by the inertness of graphite under these conditions, and by the absence of cationic species other than sodium capable of interrupting the formation of the pyro- and tectosilicate phases.

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*Dr. Nelson Maynard of the Fields and Particles Branch

During the tests in the desiccator containing carbon dioxide and saturated water vapor, the coating frosted, but at the same time maintained its integrity. Under these circumstances sodium carbonate would not be expected to form as a separate phase, but rather as a sesqui-carbonate, or mixed salt with the bicarbonate and water. At the same time, the silica would remain hydrated and could not as a result collapse into the pyro or tecto forms to promote the development of excessive tension in the film.

The undesirable effects of variable atmospheric composition can be eliminated while maintaining conductive silicate coating, $\rho d < 10^3$ ohm-meters.[2] Efforts were taken initially in this direction not only because the problem is an interesting one, but more importantly because silicate coatings outgas only water and are nonpollutive, nontoxic, and nonflammable. The key to solving the problems resided in recognizing first, that silicic acid would be the most effective buffering agent and second, that multivalent cations such as calcium would have to be added to inhibit spinoidal decompositions in a freshly prepared formulation. The mineral wollastonite was found to be a satisfactory source of calcium ions, while at the same time being capable of nucleating the precipitation of hydrated silica, and bulking the formulation effectively because of its fibrous morphology. Below are given three compositions for processing black silicate paints. In each case the ingredients are listed in Table I in the order added.

ENVIRONMENTAL STABILITY

A sample of each formulation was irradiated for 1000 hours at 10^{-6} mm Hg using an Hanovia 670A high pressure mercury lamp at a flux of one solar constant (two uv solar constants). Measurements were carried out on a Beckman DK-2A spectroreflectometer employing an in-house barium sulfate integrating sphere coating. In both cases, the final reflectance curves had shifted in the ultraviolet by an amount judged within the accuracy of the measuring capability of the instrument, and henceforth ultraviolet stable.

Flight data consists of calculations from thermal measurements to establish fluctuations in the ratio of solar absorptance to emittance (α/ϵ). Measurements were obtained from the OSO-H thermal coatings monitor experiment. Because the data are uninteresting, a listing is concluded below for but a few orbits to give some feeling for fluctuations in (α/ϵ), and their relationship to the preflight laboratory value.

Table I. Coating Formulations

MSA 87B

Ingredient	Formula I Parts by Weight	Formula II Parts by Weight	Formula III Parts by Weight	Range in Percent	Formula I Percent	Formula II Percent	Formula III Percent	Remarks
Potassium Silicate Solution	300	300	300	25 - 30	28.4	28.4	25.0	Starting from SiO_2/K_2O_{wt} 3.3 at 35% solids, silicic acid is dissolved (below)* giving SiO_2/K_2O_{wt} 5.3
Silicic Acid	51	51	51	4.3 - 5	4.8	4.8	4.3	Silicic acid: 84.5% SiO_2
Water	102	102	240	10 - 20	9.7	9.7	20.0	Slurry with 2:1 parts water
Methyl-Trimethoxy-Silane	24	24	24	1.0 - 2.1	2.3	2.3	2.0	Aids dehydration and adhesion
Black Cobalt Oxide	100	-	0	10.0 - 0	9.5	0.0	-	Colorant as well as reactive to silica
Black Iron Oxide	40	-	0	4.0 - 0	3.8	0.0	-	Colorant as well as reactive to silica
Calcium Silicate	145	271	277	14 - 27	13.7	25.6	23.1	Controls silica precipitation and bulks efficiently
Mica	13	13	1.5	0 - 1.3	1.2	12.3	0.1	Bulks efficiently
Asbestes	30	30	30.8	0 - 4.3	2.8	2.8	2.6	Bulks efficiently
Carbon Black	Molacco 36	Molacco 36 Raven 12 48	Molacco 24.6 Raven 24.6 Excelsior 12.3	3.6 - 5.0	3.4	4.6	2.0 2.0 1.0	Colorant
Talc	66	66	67.8	4.0 - 6.6	6.3	6.3	5.6	Controls silanol migration
Water	150	150	150	9.7 - 84.1	14.1	14.3	12.5	
	1057	1055	1198.6	100 - 100	100	100	100.2	*Ratios provide the optimum basis for the control of frosting.

Table II. Summary of OSO-H Thermal Coatings Data on Formula I

Orbit Number	(α/ϵ)	Remarks
0	1.14	Laboratory measurement
20	1.36	First Data Point
1119	1.40	
1935	1.40	
2449	1.37	
2109	1.35	
4195	1.32	
4955	1.32	Fluctuation ceased.

OUTGASSING TESTS*

Results of the outgassing tests are given in the table below.

Paint	Weight Loss %	VCM %
Formulation I	3.14	0.02
Formulation II	3.50	0.02

Project acceptable levels are 1 percent or less for weight loss and 0.1% or less for VCM (volatile combustible materials) at 25°C. Judged from these criteria, the VCM is more than acceptable. However, the total weight loss exceeds by substantially more than 200% the allowed amounts. Although high by project standards, the loss is low by silicate standards and as a result demonstrates why these coatings are stable in a carbon dioxide atmosphere.

ACKNOWLEDGMENT

The authors would like to express their appreciation to J. J. Triolo for making the OSO-H flight data available during the preparation of this report. The initiative and cooperation of Benjamin Seidenberg and Jules Hirschfield in supervising and editing the General Procedure in an attempt to make the technology more generally accessible is gratefully acknowledged.

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*The results in this section have been taken from a memorandum sent by Lawrence Kobren, Materials Engineering Branch to John Thole, Manager OSO Project, June 19, 1970.

APPENDIX I.

GENERAL PROCEDURE

PREPARATION AND PROCEDURES FOR GSFC MSA 87B (Clear Vehicle), MSA94B (Black Paint), MS148 and CCl PRIMERS

I. MSA87B Vehicle Formulation

Ingredient	Parts by Weight
(A) Potassium Silicate (PS-7)	300
(B) Silicic Acid (H_2SiO_3)	51
(C) Z-6070 Silane	24
(D) Water - distilled or deionized whenever water is shown	240

II. Equipment and Raw Material Sources

(A) Waring or Oster blender, home kitchen model
(B) Balance
(C) Potassium silicate PS-7, Sylvania Electric Products, Inc. Towanda, PA
(D) Silicic Acid, H_2SiO_3, Fisher Scientific
(E) Dow Corning Z6070 Silane
(F) Distilled Water

III. Blending Procedure

(A) Place PS-7 in blender
(B) While blending, add mixture of silicic acid and 200 parts water
(C) Blend at high speed until solution is clear
(D) Let cool to room temperature. Blend at high speed and slowly add Z6070. Add balance of water, blend until clear.

IV. MSA94B Paint Formulation

Ingredient	Parts by Weight*
(A) MSA87B	200
(B) Wollastonite	90
(C) Mica	0.44
(D) Asbestos	10
(E) Carbon black, Molacco	8

Ingredients	Parts by Weight
(F) Carbon black, Raven 7	8
(G) Carbon black, Excelsior**	4
(H) Talc	22
(I) Water	50

*If measured in grams, approximately 1/2 quart of vehicle or one quart of blended paint will result.

**No longer available - supplier recommends Channel Black 999 as a substitute.

V. Equipment and Raw Materials Source

(A) Waring blender
(B) Balance
(C) Wollastonite - Interpace Corp., NY.
(D) Mica- The English Mica Co., Kings Mountain, NC.
(E) Asbestos - Fisher Scientific
(F) Carbon blacks - Columbian Carbon Co., 380 Madison Ave., NY, New York, or Cities Service, Market Street, Akron, Ohio
(G) Talc - International Talc, Gouverneur, NY.

VI. Blending Procedure

(A) Place MSA87B in blender
(B) While blending, add 1/2 of Wollastonite, blend until dispersed.
(C) Add Mica and disperse
(D) Add balance of Wollastonite and disperse
(E) Add asbestos, disperse
(F) Add all carbon blacks, disperse
(G) Add talc, disperse
(H) Add water as needed. Varies from batch to batch, depending on humidity, temperature and blender speed. When paint has a smooth consistency, store in clean, poly bottles. Do Not Freeze!

VII. Preparation of GSFC CCI Primer

Ingredients	Parts by Weight
(A) Lithium Hydroxide, LiOH, Fisher	44.1
(B) Silicic Acid	216.0
(C) Water	450.0

Ingredients	Parts by Weight
(D) 31-Li33 - Prepare, utilizing A, B & C by; placing water in blender, adding LiOH while blending till solution is clear, add silicic acid while blending till solution is clear.	
(E) 31-Li33	100
(F) Potassium Silicate, PS-7	88
(G) Water	432
(H) Prepare CCI primer by placing 1/2 of water in blender, adding 31-LI33 while blending, place remaining water in clean beaker and add PS-7 while stirring Manually, add PS-7/water solution to 31-LI33/water solution while blending, blend for five minutes and store in clean poly bottle.	

VIII. Preparation of GSFC MS148 Primer

Ingredients	Parts by Weight
(A) Zinc Oxide, ZnO, SP500 Calcined	100
(B) Star Sodium Silicate, Na_2SiO_3 - Philadelphia Quartz	33.3
(C) Water	50.0
(D) Prepare MS148 primer by placing ZnO, Na_2SiO_3 and water in Waring blender. Blend until consistency is smooth. Store in clean poly bottles.	

IX. Application Procedures

(A) Painted Surfaces

(1) Abrade surface with 180 grit paper till surface is dull. If evidence of contamination is noted, abrade till metal surface is exposed.

(2) Wipe clean with damp cloth.

(3) Wipe on MS148 primer. Apply as you would polish. Avoid buildups. Wipe all loose fragments off and allow to dry a few minutes.

- (4) Apply MSA94B by laying down 2 uniform wet coats. Use Model #18 Binks pressure pot gun. Avoid dry spray.
- (5) Air supply: Dry nitrogen preferred, or filtered compressed air.

(B) Aluminum and Mild Steel (Preferred Method)

- (1) All surface treated (anodized, alodined, irridited) material to be avoided.
- (2) Abrade surface via sand blasting.*
- (3) Clean with isopropyl alcohol and dry.
- (4) Immerse substrate for 3 minutes in acid bath. Bath to consist of 88% distilled water by weight, 11% nitric acid by weight and 1% hydrofluoric acid by weight. If size rules out immersion, then applicators can be used.
- (5) Rinse with distilled water and wipe dry.
- (6) Check surface with water using water break method.
- (7) Apply paint as soon as step 5 results are satisfactory.
- (8) Alternate method: Omit step 4 when not practical, however, use primer after step 5.

*When sand blasting is not practical, "Scotch Brite" or silicon carbide paper can be employed.

(C) Stainless Steel

- (1) Sand blast (preferred) or abrade using 80 grist silicon carbide paper.
- (2) Rinse with water and dry.
- (3) Rinse off and check for "water break."

(D) Copper (No alternate method may be used)

- (1) Abrade with 180 grit silicon carbide paper or sand blast.
- (2) Remove grit with water wash.
- (3) Etch surface with 5-7% glacial acetic acid solution or 5-7% citric acid solution. Three minute etch is recommended.
- (4) Rinse with water and dry.
- (5) Check for cleanliness, via "water break" test and apply paint immediately if clean.
- (6) Repeat acid etch if required.

(E) Epoxy Fiberglass

- (1) Abrade with 180 grit silicon carbide paper until a rough surface rich in fiberglass is exposed.
- (2) Clean debris off with water.
- (3) Bake out at 50-60°C long enough to drive off most of the water.
- (4) Wipe down using CCI.
- (5) Flash off water at 100°C for approximately 15 minutes.
- (6) Spray on paint immediately after substrate has reached room temperature, otherwise primer becomes hydrophobic.

X. Cleaning and Handling

These painted surfaces, as well as any painted surface, should never be handled by bare hands. Abrade any dirty surface that should appear. If much paint has to be removed to accomplish this, then touch up must follow after the debris has been removed.

XI. Touch Up

- (A) Abrade with 180 grit silicon carbide paper to bare surface.
- (B) Clean with toluene.
- (C) Rinse with water and dry.
- (D) Dampen with water areas adjacent to abraded area.
- (E) Touch up as required.

XII. Protection

Polyethylene bagging or wrapping may take place after one week air dry at room temperature or a one hour bake at 120°C. However, since polyethylene films may have organic processing agents, it is recommended that routine cleansing using ethyl or isopropyl alcohol be employed. Dry thoroughly before using.

XIII. Shelf Life

Paint shelf life is believed to be infinite. Paints with a shelf life of three years have been sprayed successfully onto various substrates.