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THE PREPARATION AND SPACE ENVIRONMENT BEHAVIOR OF A SILICATE-TREATED ZINC OXIDE THERMAL CONTROL COATING - "101"

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MAY 1970

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INTRODUCTION

Although zinc oxide has been used as a pigment for thermal control coatings for years, it has encountered a number of serious obstacles related to its optical stability. The first of these was confirmed when the spectral reflectance of such a coating was first monitored before and after ultraviolet exposure while maintaining the vacuum environment.[1] A severe decrease in near infrared reflectance was observed which had not appeared in previous experiments in which optical measurements were made in air. The rapid reversibility of this damage upon exposure to atmospheric conditions resulted in the mushrooming development of assorted experimental techniques for performing spectral reflectance measurements in vacuum which are referred to as "in situ" measurements. The next phase in the development of zinc oxide coating occurred when it was demonstrated that the near infrared damage was eliminated when potassium silicate was used as the paint binder.[2] However, such a coating was immediately plagued with a host of practical problems such as limited shelf-life of the paint, desirability for baking the coating, and a tendency toward crazing, cracking and loss of adhesion due to the space environment. In order to rectify these problems, still another family of coatings was created. These coatings, generally referred to as S-13-G,[3] were prepared by treating the zinc oxide pigment with potassium silicate before dispersing in methyl silicone binder. In this manner, the stabilization of the infrared reflectance due to the silicate was attained while also obtaining the improved physical properties of the methyl silicone. However, it was soon realized that the alien nature of the potassium silicate as regards the methyl silicone resin (i.e., a strong base is a catalyst for polymerization of the resin) resulted in very limited shelf-life and consequent limited usefulness of the paint. Possible methods of extending usable shelf-life include removal of excess base by leaching the treated pigment, overcoating the silicate with a neutralizing material, or employing an insoluble silicate for treatment which would not contain free base.

An experimental study was made to develop a coating based on pigment treatment with an insoluble silicate and to determine the properties of such a coating. The material used for the treatment was a lithium-potassium silicate formula which was considered to be especially adaptable for this use because of its demonstrated insolubility and film forming nature.[4]

Tests were run to confirm the stabilizing influence of this silicate mixture and to determine the optimum formula for pigment treatment. The resultant coating was subjected to an exhaustive testing program including ultraviolet, electron, proton, and x-ray irradiations and thermal cycle, adhesion, and strip coat testing.

EXPERIMENTAL PROCEDURE AND TESTS

An equimolar mixture of lithium silicate and potassium silicate which forms a relatively water insensitive composite and has been used as a primer for silicate coatings (see Appendix I) was used for treatment of the zinc oxide pigment. Initially, high purity zinc oxide (New Jersey Zinc SP 500) was slurried with a water solution of this silicate mixture of sufficient concentration to yield a 7.5% silicate treatment based on dry solids. After desiccating for 24 hours at 120° C, the treated pigment was ground by mortar and pestle and a coating prepared using General Electric RTV 602 methyl silicone potting compound as a binder. The ultraviolet stability of this coating was next confirmed by "in situ" spectral reflectance measurements before and after exposure in vacuum. In order to determine the minimum silicate required for stability and thus attain maximum shelf-life, a series of pigment treatments using 3%, 1%, and 0.1% silicate solids was prepared and tested. Five samples were exposed in one vacuum chamber (10^6 torr) to radiation from an unfiltered xenon arc lamp at a total intensity of 140 mw/cm^2 sec for 230 hours. The sample plate temperature was maintained at 25°C ±3°C and the "in situ" spectral reflectance measurements obtained through the quartz window using a Beckman DK-2A Spectroreflectometer. (See Table I.)

The optimum thermal control coating (101) was next compared to other candidate thermal control coating in similar type ultraviolet tests as shown in Table II. Exposure of this coating to a variety of ionizing radiations including x-rays, 30kev electrons, and 30kev protons is shown along with the ultraviolet result as spectral reflectance curves in Figure 1. Other testing includes determination of the effect of a strippable protective coating on ultraviolet stability, thermal cycling and adhesion testing using various substrate treatments and primers (see Appendix III for recommendation).

RESULTS AND DISCUSSION

The final formulation for the thermal control coating was determined by the results of the test showing optical damage as a function of silicate solids concentration on the pigment (Table I). The stability threshold was shown to lie between 1% and 3% silicate solids and in order to assure stability, the 3% level was chosen for all subsequent development work. The designation "101" was assigned to this composition and complete instructions for its preparation are in Appendix I and II. Shelf-life tests indicate a useful refrigerated life expectancy of six weeks for this prepared coating material.

Comparison of "101" in ultraviolet tests with other thermal control coatings (Table II) show its superior stability. The results of these and other data have encouraged use of this coating on OGO-E, OGO-F, and ISIS spacecraft as well as serious consideration and testing for OAO projects.

The stability of "101" to radiation environments other than ultraviolet has been summarized spectrally in Figure 1. It can be seen that the infrared protection afforded by the silicate treatment is overridden by the high energy electron and x-ray exposures. The damage thus incurred is similar to that observed with untreated zinc oxide coatings when exposed to ultraviolet radiation. On the other hand, the proton damage which manifests itself primarily in the visible portion of the spectrum, apparently occurs by a fundamentally different mechanism. Thus, the coating has been shown to possess excellent ultraviolet resistance while remaining vulnerable to excessive damage from ionizing radiations.

Physical testing of this coating system included thermal cycling tests in vacuum from which it was discovered that very serious adhesion problems can develop when the coating is subjected to temperatures below minus 60°C. This is due to a transition of the flexible silicone binder to a brittle state at that temperature and to a subsequent incompatability of its thermal coefficient of expansion with that of the metal substrate. Considerable effort was expended to solve this problem and it is recommended that the priming and application procedures given in Appendix III be strictly followed. It is especially important where complex curved surfaces are involved, that the coating be no thicker than 8-10 mil.

The effect of application of a protective "strip coat" material (Spraylat 1071B) to prevent accidental damage to or contamination of the coating during the prelaunch phase was investigated. Strip coat material was applied to a coating sample after three days room temperature cure and subsequently removed after four weeks. Ultraviolet testing of this sample and a control which had no strip coat, yielded the following result after a 225 equivalent sun hour exposure:

$$\Delta a_s \text{ (Control)} = 0.026 \pm 0.01$$
$$\Delta a_s \text{ (Strip Coated)} = 0.019 \pm 0.01$$

Thus the strip coat had no effect on the ultraviolet stability of the coating.

CONCLUSIONS

A thermal control coating based on lithium-potassium silicate treatment of zinc oxide was formulated and shown to have a useful shelf-life of six weeks. The simplicity and ease of preparation of this coating in reproducible small batches are among its principal virtues. Special procedures were shown to be necessary to insure adequate adhesion at low temperatures.

From a spectrum of radiation damage experiments, it was shown that the coating prossesses good ultraviolet stability but can be damaged excessively by high doses of ionizing radiations such as x-rays, electrons, and protons. Thus, the usefulness of this coating for thermal control surfaces of spacecraft must be limited to missions where minimal exposures to high energy radiations can be expected.

REFERENCES

1. McKellar, L. A. et al., "Solar-Radiation-Induced Damage to Optical Properties of ZnO Type Pigments," NASA Contract No. NAS 8-11266, Lockheed Missiles and Space Company, Palo Alto, California, 1965.

2. Zerlaut, G. A., E. H. Thompkins, and H. Haroda, "Development of Space-Stable Thermal-Control Coatings (Paints with Low Solar Absorptance/Emittance Ratios," NASA Contract No. NAS 8-5479, IIT Research Institute, Chicago, Illinois, 1963.

3. Zerlaut, G. A., F. O. Rogers, and G. Noble, "The Development of S-13-G-Type Thermal Control Coatings Based on Silicate-Treated Zinc Oxide," AIAA 3rd Thermophysics Conference, Los Angeles, California, June 1968.

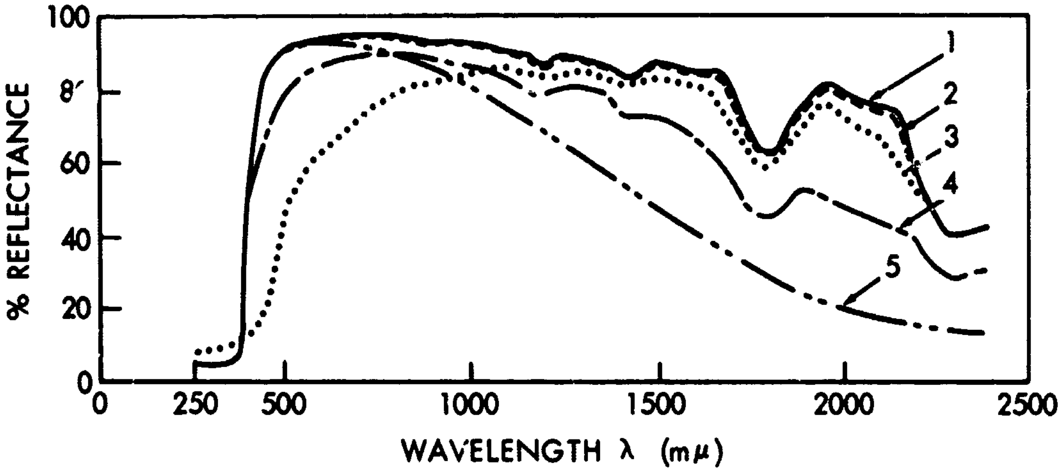
4. Stuart, John W., GSFC, Thermophysics Branch, Personal Communication, 1967.

Table I
Effect of Varying Silicate Concentration on Ultraviolet Stability of Coating

Paint	Wt. % Silicate	$\alpha_{s_{\text{Initial}}}$	$\alpha_{s_{230\ \text{ESH}}}$	$\Delta\alpha_s$
#88	No Silicate	0.180	0.197	0.017
#103	0.1%	0.171	0.194	0.023
#102	1.0%	0.211	0.220	0.009
#101	3.0%	0.199	0.193	-0.006
#100	7-1/2%	0.202	0.196	-0.006

Table II
Comparison of Ultraviolet Stability of 101 with other Thermal Control Coatings

Paint	Unfiltered Xenon 140 mw/cm^2 sec Sample 25°C			Filtered Xenon X-25 Solar Simulator 21°C		
	α_{Initial}	$\alpha_{193\ \text{hrs}}$	$\Delta\alpha_{193\ \text{hrs}}$	α_{Initial}	$\alpha_{204\ \text{hrs}}$	$\Delta\alpha_{204\ \text{hrs}}$
Tempil Corp. Pyromark	0.297	0.396	0.099	0.281	0.361	0.080
Dow Corning Q92-007	0.184	0.258	0.074	—	—	—
101-1B	0.182	0.172	-0.010	0.167	0.187	0.020



Curve Identification:

———————— #1 Initial reflectance

- - - - - - - - - - #2* 240 UV hrs, xenon lamp, "in situ" measurement

.... #3* 10^{16} p/cm^2, 30 kev protons, air measurement

——— – ——— #4* 10^{16} e/cm^2, 30 kev electrons, air measurement

——— -- ——— #5 17 x 10^{16} kev/cm^2, x-ray dose, from copper target, "in situ" measurement

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*Test results from E. M. R. under contract No. NAS 5-9469

Figure 1. Effect of Various Radiations on Spectral Reflectance of Silicate-treated ZnO Coating "101"

APPENDIX I

PREPARATION OF THE SILICATE-TREATED ZINC OXIDE PIGMENT

Materials

Zinc Oxide	500 grams	New Jersey Zinc Co. SP 500
Lithium Silicate	68.8 grams	Du Pont Polysilicate "48"
Distilled Water	81.2 grams	
Lithium Silicate Solution	150.0 grams	
Potassium Silicate	43.0 grams	Sylvania PS-7 Electronic Grade
Distilled Water	107.0 grams	
Potassium Silicate Solution	150.0 grams	

Procedure

The lithium and potassium silicate solutions are stirred together over night. Sufficient distilled water is added to the zinc oxide powder to make a thin slurry. The silicate mixture is added and the resultant slurry is stirred 24 hours before removal of water. Water is driven off by heating in a circulating air oven at 110°C with occasional stirring. When the treated pigment appears dry it is crushed by mortar and pestle followed by heating three hours at 160°C.

The pigment material is now ready to be formulated into a coating.

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APPENDIX II
COATING PREPARATION PROCEDURE

Materials

Silicate-Treated pigment	300 grams	Appendix I
Methyl Silicone Resin	150 grams	General Electric RTV 602
Toluene	110 ml	Reagent Grade

Procedure

The coating is most easily prepared using a common kitchen blendor such as Waring or Osterizer. Combine the silicone resin and 70 ml of toluene in the blendor and stir briefly. Add the pigment slowly while the blendor is on low speed. After the pigment is completely wetted, blend on high speed for five minutes. The blendor jar is then immediately immersed in cold water for five minutes to cool the contents. This is followed by another similar blending and cooling cycle. The remaining 40 ml of toluene is added and blended in for about one minute. The coating is filtered through a 170 mesh filter to remove large particles. It is now ready for use and should be stored in a refrigerator if immediate application is not contemplated. For optimum results apply in accordance with the recommendation in Appendix III.

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APPEXDIX III
PROCEDURE FOR APPLICATION OF THERMAL CONTROL COATING "101"

1. Clean substrate material free of grease, dirt, etc.

2. Abrade surface lightly with sandpaper or steel wool.

3. Clean substrate again with appropriate solvent. (Acetone, MEK, Toluene, etc.)

4. Apply by spray technique, Nextel Brand, Velvet Coating 401-A10 White, 3 M Company, as a prime coat - dry thickness should be about 3 mil. This material must be cured by one of the following methods.

   A. Let cure at room temperature 24 hrs., or

   B. Let dry one hour at R. T. followed by heating to 150°F 2 hours.

5. One hour before application of paint, spray on a <u>thin</u> coating of GE Primer SS4044. Amount to apply would be the same as would be necessary to wet a non-porous surface. In this case the surface is porous and this primer will soak in.

6. Paint must be refrigerated when not being used. Bring to room temperature before use and stir thoroughly.

7. Paint must be catalyzed before use with 2% of the furnished catalyst. Catalyst consists of 0.2 grams Tetramethyl Ammonium Hydroxide per milliliter of isopropyl alcohol.

8. Apply "101" coating by standard spray technique to achieve about 8-10 mil thickness. Thin if necessary with toluene.

9. Paint must be cured at room temperature 24 hours before handling and one week before degradation testing.