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3. Electrically Conductive Paints for Satellites

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Abstract

A program was conducted to develop and test electrically conductive paint coatings for spacecraft. A wide variety of organic and inorganic coatings were formulated using conductive binders, conductive pigments, and similar approaches. Z-93, IITRI's standard specification inorganic thermal control coating, exhibits good electrical properties ($\sim 10^9$ ohms) and, of course, is a very space-stable coating system. Several coatings based on a conductive pigment (antimony-doped tin oxide) in silicone and silicate binders offer considerable promise. Paint systems using commercially available conductive polymers also appear to be of interest, but will require substantial development. Evaluations were made based on electrical conductivity, paint physical properties, and the stability of spectral reflectance in space environmental testing.

1. INTRODUCTION

In traversing those regions of space where energetic charged particle fluxes exist, a spacecraft may acquire a very large electrical potential.[1,3] Because the

instantaneous incident flux will vary (with time) in magnitude, energy, and composition, the environment is a dynamic one; the resulting charge buildup also varies with time.

Space Charge Accumulation (SCA) represents a serious threat to spacecraft performance; at high electrical potentials it poses the threat of electrical discharge with resultant material damage and an rf burst. At low potentials, in certain applications, SCA interferes with measurements of the electrical environment. On some spacecraft even very small differences in potential from one point to another can seriously degrade the sensitivity of instrumentation to incident charged particle fluxes. The greater the potential, the greater is the disparity in the measurement. The SCA problem then is either the moderate one of reducing SCA to levels at which electrical discharge is highly improbable or the more difficult one of developing serviceable materials with sufficiently high electrical conductivity to eliminate high electrical potentials.

The underlying problem in this program is that the "standard" requirements placed on lo α_s/ϵ systems are not compatible with the concurrent requirement for high electrical conductivity. Solar absorptance, in fact, generally parallels electrical resistivity. Nonetheless, because all external surfaces of a spacecraft have a thermal control function, the essence of the SCA problem is to achieve high electrical conductivity in surface materials without seriously compromising thermal radiative properties and performance.

In this program we have investigated several approaches to the SCA problem—all from a materials standpoint. The objective may be stated rather simply: to identify surface materials with high electrical conductivity and acceptable optical and physical properties. Although quantitative criteria and objectives were not specified, the general requirements of satisfactory surface coatings are shown in Table 1.

Table 1. Desirable Properties of High Electrical Conductivity Thermal Control Coatings

Property	Desirable Value
Solar Absorptance, α_s	< 0.4
Thermal Emittance, ϵ	> 0.8
Electrical Conductivity	~ 10^9 ohms
Optical Stability, $\Delta\alpha_s$	< 0.1/5-10 years
Outgassing/Contamination	< 10^{-5} gm/cm^2-year

2. TECHNICAL DISCUSSIONS

2.1 Statement of the Problem

The successful development of a conductive paint system for spacecraft appli-
cations requires that the resistivity of the dielectric materials which comprise
them be reduced. The scope of th: program includes all pigmented coatings and
surface materials, except those applied by adhesives or by similar techniques.
To increase the conductivity of a paint coating, the usual approach is to use a highly
conductive pigment, for example, carbon black. This latter approach, however,
would lead to a paint with very high α_s/ϵ.

The incorporation oi metal pigments in paints to decrease electrical resistivity
has been largely unsuccessful, because pigments remain in the dispersed phase.
Thus, the incorporation of metal, semiconductive, or highly conducting pigments
in resins will almost inevitably encounter the problem of wetting. In "successful"
paint binders, the pigment particles will be 100 percent wetted and thus become
physically and electrically isolated by the binder.

The very nature of a paint—a dispersed pigment or pigments (discontinuous
phase) in a binder (continuous phase) suggests that the binder be made conductive.
The overall problem, therefore, is to produce a paint coating whose binder is elec-
trically conductive or whose pigment has such a character that it can, via stringing,
flocculation, hydrogen binding, etc., effectively form a continuous filament.

The problem, apart from any environmental stability or other practical con-
siderations, is that increased electrical conductivity in organic materials is gener-
ally accompanied by increased optical absorption (decreased transparency). In
simple but fundamental terms, electrical conductivity arises from the motion of
electrons in the conduction band. Transparency, the absence of absorption, arises
from the very low probability of transitions to the conduction bands. The further
apart are the valence and conduction bands, the less the probability of an electron
reaching the latter, and accordingly both the electrical conductivity and optical
absorption will be low. Conversely, the closer these bands, the more likely that the
material will be colored, possibly even black, and also that it will have high elec-
trical conductivity. In short, the fundamental properties giving rise to high trans-
parency in a dielectric material are the same ones which underlie its high resistiv-
ity. One should not conclude that transparency and conductivity are mutually
exclusive, but rather that some compromises may be necessary.

2.2 General Approaches

A great number of conductive materials are available, many commercially,
some in limited experimental quantities, and still others only by synthesis. The

general approach involved a search for these materials—resins, pigments, fibers, etc. —preliminary determination of their properties and availability, and a series of experimental studies to evaluate their feasibility. Conductive polymers, both organic and inorganic, received primary attention.

The enhancement of conductivity in IITRI's specification thermal control coatings, S-13G/LO and Z-93, production and evaluation of conductive pigments, fibers, and the synthesis and evaluation of conductive polymers were important elements in the program.

The program took three general directions: Conductive Organic Polymers, Conductive Inorganic Binders, and Conductive Pigments. In each approach, attempts were made to obtain commercially available materials or, if the preparative route was simple and direct, to synthesize them.

2.3 Conductive Organic Polymers

Many potential materials were identified but most of the materials were rejected because they are highly colored or black, carbon-pigmented materials, aerosol antistats, or similar materials which are not in a useful form. Five quaternary ammonium chloride polymers and poly(vinyl carbazole), PVK, were investigated as binders which possess conductive or photoconductive properties. The five cationic polymers were: DeSoto C-112, the diquaternary salt of α,α' - dichloroxylene and N, N, N', N' - tetramethylethylene diamine; DeSoto C-112, the methyl chloride quaternary salt of poly(4-vinyl pyridine); DeSoto C-113, the trimethylamine quaternary salt of poly(epichlorohydrin); Dow ECR-34, the trimethylamine quaternary salt of poly(4-vinyl benzyl chloride); Merck 261, the methyl chloride quaternary salt of poly(diallyl n-ethyl amine).

The conductive polymers chosen for evaluation in this program were originally developed as conductive treatments for paper in the electrophotographic copy industry. These polymers are used to increase the conductivity of the paper base stock and to dissipate the corona induced surface charge in the light imaging process.[4,5] PVK, a photoconductive polymer, has also been utilized to dissipate charge under light imaging conditions in the electrophotographic process. PVK is of interest because of its conductive properties when illuminated with photons from an ultraviolet light source (~360 nm). PVK has a conductivity of 10^{-13} ohm^{-1} cm^{-1} when exposed to an ultraviolet light source and a dark conductivity of 5×10^{-16} ohm^{-1} cm^{-1}. The addition of dopants an' formation of charge transfer complexes with PVK has been shown to shift the absorption spectrum into the visible region, resulting in increased conductivity in the same region (~ 10^{-13} ohm^{-1} cm^{-1} at 550 nm).[7,8]

2.3.1 FILM STUDIES

Film studies on Dow ECR-34 indicated that films applied at relatively low humidities developed hairline cracks upon drying. Conditioning of the films during drying at 50 percent relative humidity provided initial films for surface and volume resistivity measurements.

Films of Dow ECR-34 (as received), cast from solution, developed craters and showed inhomogeneous coverage of the aluminum substrate (Alclad 2024 T3, hot alkaline cleaned). The source of this behavior was attributed to the high surface tension of the aqueous solution of the Dow ECR-34, ~57 dynes/cm^2.

In the preparation of Merck 261 films, it was observed that drying these films at 50 percent relative humidity resulted in tacky films. This material shows film-forming properties similar to those of the Dow ECR-34. The surface tension was determined to be 72-74 dynes/cm^2. Triton X-100, a nonionic surfactant was added to improve film formation characteristics prior to making electrical measurements.

Films of PVK, with and without film forming aids, with various levels of crystal violet (CV) dye added (2.5×10^{-7} to 2.5×10^{-5} mole per gram PVK) were prepared. The presence of film forming aids is necessary for the CV to completely dissolve in the present system.

A solvent system compatible with both the PVK and 2,4,7 trinitro-9-fluorenone (TNF) was found. Films of the 1:1 (mole) complex of PVK and TNF were cast.

2.4 Electrical Measurements

Surface and volume resistivity measurements were made or attempted on all of the coating candidates. In general, IITRI accomplished the measurements on the inorganic materials while DeSoto, Inc. made measurements on the organic system. DeSoto made all of the charge acceptance measurements.

The resistivity-measuring equipment used by IITRI consists of a Hewlett-Packard Model 4329A High Resistance Meter used in conjunction with an HP Model 16008A resistivity cell.

At DeSoto, Inc., electrical property measurements were made with a Keithley 615 Digital Electrometer and 246 High Voltage Supply coupled with a 6105 Resistivity Adapter. These three components permit the measurement of the volume and surface resistivities of materials in accordance with ASTM D257-66 "Standard Method of Test for Electrical Resistance of Insulating Materials." The determination of the surface and volume resistivity in this method assumes the validity of Ohm's law for the materials tested.

2.4.1 CONDUCTIVE ORGANIC POLYMERS

Surface resistivity measurements were made at 5 percent relative humidity on the various polymer films prepared for this program. The results of these

measurements are summarized in Table 2. For the conductive polymers tested the surface resistivities fall into a rather narrow range ($\sim 10^{11}$ ohms). Polyvinyl carbazole (PVK) and modified films of PVK exhibited resistivities approximately one or two orders of magnitude higher than the conductive polymers.

Table 2. Surface Resistivities of Polymer
Films 25°C at 5% Relative Humidity

Material	ρ_s (ohms)
DeSoto C-111	2.4×10^{11}
DeSoto C-111[a]	$2.4-2.6 \times 10^{11}$
DeSoto C-112	1.6×10^{11}
DeSoto C-113[b]	1.7×10^{11}
Dow ECR - 34[c]	$1.3-3.8 \times 10^{11}$
Merck 261[d]	$1.8-2.4 \times 10^{11}$
PVK	2.2×10^{13}
PVK with filming aids	2×10^{11}
PVK + DV[e] + filming aids	$2 \times 10^{12} - 2 \times 10^{13}$
PVK + CV[e]	$2.2 \times 10^{11} - 1.3 \times 10^{14}$
PVK + TNF[f]	$9 \times 10^{11} - 9 \times 10^{12}$

a. Triton X-100 (Rohm & Haas), a nonionic surfactant, was added at 0.002g/g C-112 polymer.

b. Amaizo 745 D (American Maize Products Co.); used at 0.25g/g polymer.

c. Triton X-100 was added at 0.013g/g polymer.

d. Triton X-100 was added at 0.003g/g polymer.

e. Concentration of crystal violet (CV) in PVK ranged from 2.5×10^{-7} to $2.5 + 10^{-5}$ mole/g PVK.

f. A 1 to 1 molar complex of trinitrofluorenone (TNF) and PVK.

The surface resistivity values obtained for the quaternary ammonium polymers are consistent with known effects of relative humidity on resistivity. The surface resistivity increases with a decrease in relative humidity.[4,9,10] A comparison of the surface resistivities at differing humidities is shown in Table 3.

Several attempts were made to measure the volume resistivity of the thin polymer films on aluminum. With the impressed voltage at 500 V, the power supply became overloaded and no measurements could be recorded. Attempts were made to determine the volume resistivity at lower voltages but these efforts were also

hampered by frequent overloading. In the film thickness range studied, the films were sufficiently conductive to bleed the impressed charge to ground under the experimental conditions.

Table 3. Surface Resistivity of Quaternary Ammonium Polymers at Various Relative Humidities

Polymer	Concentration (lb/3000 ft^2)	Surface Resistivity ρ_s, ohm (% R.H.)		
		46%	13%	5%
DeSoto C-111	1.25	3.8×10^8	5.2×10^9	2.5×10^{11}
DeSoto C-112	0.8	2.5×10^7	3.4×10^9	1.6×10^{11}
DeSoto C-113	1.5	1.9×10^{7a}	1.9×10^{9b}	1.7×10^{11}
Dow ECR-34	0.9	5.0×10^7	7.3×10^8	2.6×10^{11}
Merck 261	1.3	3.7×10^7	4.2×10^9	2.1×10^{11}
a. 50% Relative Humidity.		b. 17% Relative Humidity.		

2.4.2 INORGANIC BINDERS

The inorganic binders evaluated are soluble alkali silicates. Potassium, lithium, and sodium silicates were obtained from commercial suppliers for evaluation. They are listed in Table 4.

Table 4. Alkali Metal Silicates

Trade Name	Supplier	Weight Ratio $M_2O:SiO_2$
SODIUM SILICATES:		
S 35	Philadelphia Quartz	1:3.75
N	Philadelphia Quartz	1:3.22
K	Philadelphia Quartz	1:2.90
RU	Philadelphia Quartz	1:2.40
B-W	Philadelphia Quartz	1:1.60
POTASSIUM SILICATES:		
KASIL No. 1	Philadelphia Quartz	1:2.50
KASIL No. 6	Philadelphia Quartz	1:2.10
LITHIUM SILICATES:		
LITHSIL-4	Lithcoa	1:9.41
LITHSIL-6	Lithcoa	1:11.7
LITHSIL-5	Lithcoa	1:6.53

A broad range of silicates with varying alkali-to-silicate ratios are shown. As reported in the literature,[11] increasing electrical conductivity may be expected with increasing alkali content.

Considerable difficulty was experienced in making measurements with repeatable results. A temperature-humidity conditioning procedure and close observance of measurement procedures were necessary. Table 5 presents electrical measurement data for a series of inorganic paints under ambient humidity conditions. In view of the uncertainty in the measurement accuracy, the expected trend is not evident, and it appears that only a slight advantage might occur in the use of sodium silicate rather than potassium or lithium silicate-binders.

Table 5. Summary of Electrical Measurements for Conductive Inorganic Coatings

Binder	Surface Resistivity (ohm)	
	ZnO Pigmented	Zn_2TiO_4 Pigmented
$Na_2O:SiO_2$		
PQ S-35	7.7×10^8	1.7×10^9
PQ B-W	8.5×10^8	---
$Li_2O \cdot SiO_2$		
Lithsil No. 4	2.4×10^9	3.6×10^9
Lithsil No. 6	1.2×10^9	3.8×10^9
$K_2O \cdot SiO_2$		
Kasil No. 1	---	2.4×10^9

All of these coatings exhibit good adhesion, good whiteness and no indication of cracking, and thus can be considered for further evaulation (and improvement) as low α_s/ϵ coatings. The "standard" inorganic coatings exhibit low and rather consistent resistivity values.

2.4.3 CHARGE ACCEPTANCE MEASUREMENTS

The surface charge acceptance measurements were made according to procedures common to the electrophotographic industry in the evaluation of photoconductive paper.[4] A high voltage corona (3-5 kV) is used to induce a charge on the surface of the films. Experimentally, the voltage induced in a probe is measured, not the charge density. It can be shown, however, that a simple relationship exists between the voltage on an infinite plane at distance r, and the charge density, σ

$$v = \frac{\sigma}{r} \ . \qquad\qquad (1)$$

The charge density is directly proportional to the voltage at a fixed distance.

The probe used in the work reported here was calibrated by using the Keithley 246 High Voltage Power Supply as a source of constant voltage. In general, the charging of films with a corona wand provides a saturation voltage, that is, the maximum voltage capable of being accepted by a given polymer film. After charging is discontinued, the voltage impressed upon the film gradually decays to ground potential. The rate at which the charge dissipates depends on the electrical characteristics of the material and the external conditions. For electrical insulators the decay rate may be infinitesimally slow. For photoconductors, such as PVK, light illumination greatly increases the decay rate and for conductive polymer films often no charge buildup is observable. Surface charge measurements are recorded for a variety of materials in Table 6 using a negative corona at 5 percent relative humidity.

Table 6. Surface Charge Acceptance Measurements of Clear and Pigmented Coatings

Material	Corona Current - Time	Probe Reading (volts)
DeSoto C111	0. 1mA, 30 sec	0
Dow ECR-34	0. 1mA, 30 sec 0. 2mA, 30 sec	0 0
Merck 261	0. 2mA, 30 sec	0
PVK	0. 1mA, 30 sec	-35
PVK + CV	0. 1mA, 30 sec	-30
PVK + TNF	0. 1mA, 30 sec 0. 1mA, 60 sec	0 0
S-13G/LO (8. 5 mil)[a]	0. 1mA, 30 sec 0. 1mA, 60 sec 0. 1mA, 60 sec	-29 -48 -200
RTV-602 (1. 5-3. 5 mil)[a]	0. 1mA, 60 sec	-422
Z-93 (3. 4 mil)[a]	0. 1mA, 60 sec	0

a. Materials supplied by IIT Research Institute.

At the request of the Air Force Materials Laboratory, samples of aluminized FEP Teflon (2 mil), aluminized Kapton (1 mil), and Astroquartz fabric (style 581, heat treated 3 hours at 800°C) were evaluated for surface charge acceptance in the same manner as the conductive polymers and thermal control materials. The data for these materials are presented in Table 7. A static charge may have been developed during the handling of the samples in the dry box. The voltages developed

in the Teflon FEP and Kapton materials were lower than expected. These same materials were tested in the 6105 Resistivity Adaptor at + 500 V in the volume resistivity mode. For the Teflon FEP the effective resistance was ~1.7 × 10^{11} ohm; and for Kapton, ~1.2 × 10^{12} ohm. The Astroquartz material registered an effective resistance of ~5 × 10^{13} ohm.

Table 7. Surface Charge Measurements of Plastic Materials

Material	Current - Time	Probe Reading (volts)
Teflon FEP (2 mil), polymer side	0.1mA, 30 sec	-80
	0.1mA, 60 sec	-94
	0[a]	-97
Teflon FEP (2 mil), metal side	0.1mA, 30 sec	-130 ___
	0.1mA, 60 sec	+73
	0.2mA, 60 sec	+68
	0[a]	+73
Kapton (1 mil), metal side	0.1mA, 30 sec	-102
	0.1mA, 60 sec	-52
	0.2mA, 60 sec	+2
	0[a]	+43
Kapton (1 mil), polymer side	0.1mA, 30 sec	-57
	0.1mA, 60 sec	-50
	0.2mA, 30 sec	-45
	0[a]	-70
Astroquartz	0.1mA, 30 sec	-312
	0.1mA, 60 sec	-506
	0[a]	+435

a. Readings obtained before exposure to corona current; charge induced by handling material.

During the course of measuring the surface charge of the various polymer systems, the power supply voltage exhibited some variation between 3-5 kV. Accordingly, the data in Tables 6 and 7 should be viewed as qualitative in nature.

2.5 Conductive Paint Systems — Coatings Evaluation

A large number of clear and pigmented films of both the organic and inorganic polymers were prepared for evaluation as films and coatings. Many, if not most, of the organic formulations were found to be unsuitable. DeSoto polymers C-112 and C-113, for example, are too low in molecular weight to be good film formers and remain liquid. Some films would adhere to aluminum substrates only if

pigmented; others, only without pigmentation. Adhesion is a major problem for many of these coatings; another is compatibility with solvents (aqueous and organic). Since RTV 602/LO is a space-qualified paint binder, we attempted to modify it electrically by "doping" it with DeSoto and commercial polymers. These attempts were completely unsuccessful because of immiscibility.

The intent of these laboratory efforts was to determine which candidate materials, or combinations of them, would be most useful as practical conductive coatings. Table 8 presents surface resistivity data pertaining to some of the more useful coatings. These coatings are grouped in several categories. The first, of course, contains IITRI's two specification coating systems, S-13G/LO and Z-93. The second group illustrates the difficulty, mentioned earlier, in overcoming the wetting problem, even with highly conductive pigments. The third group is composed of a specially developed conductive pigment (a SnO_2:Sb pigment developed under AF Contract No. F33615-72-C-1657), in silicone and silicate binders. The next group is made up of zinc oxide and zinc orthotitanate pigmented silicate coatings; in this case, the pigments are space-qualified and the silicate binders are experimental. The final group shows the only two employing conductive polymers that have some potential for use as practical low α_s/ϵ thermal control coatings.

As can be seen in the first group, the ZnO pigmented silicate, Z-93, possesses relatively good conductivity, but the ZnO-pigmented silicone, S-13G/LO does not. The metal pigmented silicones further illustrate the "wetting" problem.

The conductivity of the antimony-doped tin oxide (SnO_2S_b) pigment is very good. It should be noted, however, that the conductivity of coatings containing this pigment depends sensitively on pigment volume concentration (PVC). Especially of interest is the very large change in conductivity in RTV602 coatings with only a doubling of the PVC. This contrasts sharply with the observations above that RTV602 cannot be made conductive by pigmenting it with conductive pigments.

Table 8. Summary of Electrical Measurements

Materials Description	Surface Resistivity (ohms)
Conventional Coatings	
S-13G/LO	1.5×10^{13}
Z-93	4.5×10^{8}
Leafing Metal-Pigmented Silicones	
Al. Powder/RTV602	3.2×10^{12}
ZN Powder/RTV602	1.6×10^{13}
Cu Powder/RTV602	4.8×10^{14}

Table 8. Summary of Electrical Measurements (Cont)

Materials Description	Surface Resistivity (ohms)
Antimony-doped Tin Oxide Coatings	
SnO_2:Sb/RTV602 (low PVC)	2.8×10^{13}
SnO_2:Sb/RTV602 (high PVC)	1.2×10^9
SnO_2:Sb/PS-7 (low PVC)	1.2×10^8
SnO_2:Sb/PS-7 (high PVC)	2.1×10^7
Inorganic Coatings	
ZnO*/Na_2SiO_3 (S-35)	7.7×10^8
ZnO*/Na_2SiO_3 (B-W)	8.5×10^8
ZnO*/Li_2SiO_3 (Lithosil 4)	2.3×10^9
ZnO*/Li_2SiO_3 (Lithosil 6)	1.2×10^9
$Zn_2TiO_4$7K_2SiO_3 (Kasil 1)	2.4×10^9
Zn_2TiO_4/Li_2SiO_3 (Lithosil 4)	3.6×10^9
Zn_2TiO_4/Li_2SiO_3 (Lithosil 6)	3.8×10^9
Zn_2TiO_4/Na_2SiO_3 (S-35)	1.7×10^9
Conductive Organic Coatings	
S-13G Pigment/Merck No. 261	3.4×10^6
S-13G Pigment/Dow ECR-34	2.2×10^6

*Calcined.ZnO

3. SPACE SIMULATION TESTS AND RESULTS

The determination of which coatings would be evaluated for ultraviolet radiation stability was made on the basis of many evaluations, including electrical properties, optical properties, appearance, integrity, coating and film-forming properties, and adhesion. Three tests were conducted in the Combined Radiation Effects Facility (CREF). The first contained a series of primarily organic-based coatings; the second, inorganic coatings; and the third, the coatings which performed best in the first two.

In all of these tests the reflectance spectra of all samples were measured in-situ before and after irradiation. The spectra were recorded in the range 325 to 2600 nm. The ultraviolet radiation source employed is a Hanovia 5000W Mercury-Xenon burner, which illuminates the samples at an equivalent solar UV intensity of 4X. The spectral data at specific wavelengths is shown in Tables 9, 10, and 11.

3.1 CREF Test No. 19 — Results

Table 9 lists the sample materials and the in situ before-and-after-test reflectance values at selected wavelengths. Standard S-13G and Z-93 coatings were included in this test for reference. Total UV exposure was 256 ESH. Reflectance spectra for the Dow and Merck clear films were recorded in the wavelength interval 250 to 2600 nm. These two samples, however, disintegrated in establishing vacuum conditions.

Table 9. CREF Test No. 19 — Test Results

Sample Description (Pigment/Binder)	Exposure (ESH)	Reflectance Values (%)			
		R_{400}	R_{600}	R_{800}	R_{1000}
MERCK No. 261*	Disintegrated in vacuum before irradiation				
PVK-Crystal Violet*	0 256	11 11	11 30	11 30	58 53
PVK-Trinitrofluorenon*	0 256	10.5 10.5	10.5 10.5	51 51	62.5 62.5
PVK*	0 256	54 23	61 54	58.5 57.0	68 67
DOW ECR-34*	Disintegrated in vacuum before irradiation				
S-13G Pigment/DOW ECR-34	0 256	76 62	90 86	88.5 87.0	88 86.5
S-13G Pigment/DeSoto C-111	0 256	63 52	70.0 66	56 53	44 41
AFML** Pigment/RTV 602	0 256	63 52	71.5 67	61 58	48 46
AFML** Pigment/PS-7	0 256	73 69	81.5 78.5	76 73	66.5 65
S-13G Pigment/MERCK	0 256	74 73	87 86	87 85.5	87 85.5
S13G	0 256	79 77	92.5 91.0	92.5 91	91 90
Z-93	0 256	83.5 82	95 94	95.5 94	95 94.5

*Transparent, unpigmented films.

**AFML Pigment is electrically conductive antimony-doped tin oxide (SNO_2:Sb) supplied by AFML.

It is obvious from the table that most of the coatings tested are highly unstable. The degradation of Z-93 and of S-13G/LO, particularly the unusual character of the spectral changes, suggest substantial contamination. The photo-decomposition of the Dow and DeSoto polymers is strongly suspected. Apart from the specifica-

tion coatings, the coating of S-13G pigment in Merck No. 261 shows good initial properties and reasonable UV-stability. Even though relatively stable, the doped PVK films exhibit unacceptable absorption. The behavior of the undoped PVK film contrasts slightly with that observed in another program where highly purified PVK was used. In this study the PVK contained a film-former additive. Consequently, the observed degradation may be due to impurities - and possible to contamination from other samples.

3.2 CREF Test No. 20

This test is similar to the previous one except that it contained only inorganic samples. Z-93, in this test also, was included for reference purposes. As expected, the inorganic coatings sustain comparatively minor degradation. Furthermore, the spectral changes in Z-93 are not quite characteristic, suggesting that some of the contamination from the previous irradiation test remained in the CREF, apparently, to increase the damage.

The samples in CREF Test No. 20 were exposed under vacuum $(P < 2 \times 10^{-7}$ Torr) to a total of 204 ESH of simulated solar ultraviolet radiation.

Table 10. CREF Test No. 20 - Results

Sample Description (Pigment/Binder)	Exposure (ESH)	Reflectance Values (%)			
		R_{400}	R_{600}	R_{800}	R_{1000}
ZnO/S-35	0	68	90	89	88.5
	204	75	88.5	87	87
ZnO/Lithosil 6	0	73	91	90	89
	204	68	87	87	87
ZnO/Kasil 1	0	79	91	91	90
	204	78	90	91	90
ZnO/Lithosil 4	0	72	90	88.5	87.5
	204	70	88.5	88.5	87.5
Z-93	0	71	92	92.5	92
	204	71	90	92	92
ZnO/W-W Silicate	0	66	88	89	88
	204	66	88	88	87
ZOT/Kasil 1	0	80	84	83.5	82
	204	77	83	84.5	84
ZOT/(S-35)	0	80	88	87	86.5
	204	77	87	89	88
ZOT/OS-7	0	81	87	86.5	35
	204	78	85.5	88.0	87
ZOT/Lithosil 4	0	93	88.5	83	77.5
	205	80	87	84	78.5
ZOT/B-W Silicate	0	82	88	88	87.5
	204	78	86	90	90
ZOT/Lithosil 6	0	84	90	90	90
	204	80	88	92	91.5

The abbreviations in Table 10 are described as follows:

ZnO	Calcined SP-500 Zinc Oxide (New Jersey Zinc)
ZOT	Zinc Orthotitanate. IITRI Batch No. LH-101 precalcined at 600°C/2 hr, calcined at 900°C/2 hr
S-35	Sodium Silicate, Philadelphia Quartz Co. No. S-35
B-W	Sodium Silicate, Philadelphia Quartz Co. No. B-W
Kasil-1	Potassium Silicate, Philadelphia Quartz Co. Kasil No. 1
Lithosil-4	Lithium Silicate, LITHCOA, Inc., Lithosil No. 4
Lithosil-6	Lithium Silicate, LITHCOA, Inc., Lithosil No. 6
PS-7	Potassium Silicate, Sylvania Elec. Co., No. PS-7
DOW	Dow Chemical Co. Electroconductive Resin ECR-34
MERCK	Merck Chemical Co. Electroconductive Resin No. 261
S-13G Pig	Potassium Silicate Encapsulated SP-500 ZnO- the pigment used in S-13/LO thermal control coating

3.3 CREF Test No. 21

Those samples which exhibited the best initial properties and UV stability in the two previous tests were selected for testing in CREF Test No. 21. They are listed in Tables 11 and 12 along with pre- and post-test reflectance data at selected wavelengths.

Table 11. CREF Test No. 21 - Results

Sample Description (Pigment/Binder)	Exposure (ESH)	Reflectance Values (%)			
		R_{400}	R_{600}	R_{800}	R_{1000}
S-13G PIG/MERCK	0	79	91	91	92
	180	76	88	88	88
	558	77	89	89	90.5
	1032	79	90.5	90.5	91.5
S-13G PIG/DOW	0	74	89	89.5	88.5
	180	65	84.5	86	85
	558	67	88	89.5	88.5
	1032	61	83.5	90	89
ZnO/Lithosil 6	0	70	91	92	91
	180	69	86	88	87
	558	73	91	92	91
	1032	73	91	93	91.5
ZOT/Kasil 1	0	80	86	87	85
	180	75	81	82.5	81.5
	558	78	84.0	84.5	84.5
	1032	78	84.5	87	85
ZOT/S-35	0	81	88	89.5	88.5
	180	78	87.5	88	88
	558	77	87.5	88	87
	1032	77	87.5	89.5	88.5

Table 11. CREF Test No. 21 - Results (Cont)

Sample Description (Pigment/Binder)	Exposure (ESH)	Reflectance Values (%)			
		R_{400}	R_{600}	R_{800}	R_{1000}
ZOT/Lithosil 6	0	85	90.5	92	91.5
	180	82	88	81	90.5
	558	81	86.5	89	88.5
	1032	80.5	88	92	91.5
ZnO/B-W	0	71	89	91	
	180	71	89	91	
	558	71	89	90.5	
	1032	71	89	92	
ZOT/Lithosil 4	0	84	89	89.5	89.5
	180	81	87	89	88.5
	558	81	87	89	38.5
	1032	81	87	89.5	89.5

In this test the samples were exposed in vacuo ($P < 2 \times 10^{-7}$ Torr) to a total of 1032 ESH at a nominal intensity of four (4) equivalent suns. Reflectance spectra in the wavelength range from 325 to 2600 nm were taken after nominal exposures of 180, 550, and 1000 ESH. After a careful review of these spectra it was concluded that the anomalous behavior of the 180 ESH data is due to contamination. The remainder of the data follow the trends we expect. It is quite possible that the contamination resulted from the photodecomposition of the S-13G/DOW ECR-34 coating.

Table 12. CREF Test No. 21 - Results

Sample Description (Pigment/Binder)	Exposure (ESH)	Reflectance Values (%)			
		R_{400}	R_{600}	R_{800}	R_{1000}
ZnO/S-35	0	67	92	94	93
	180	70	92	89.5	87.5
	558	67	91	93.0	92
	1032	67	91	94	93
ZnO/Lithosil 4	0	38	89	90	88
	180	71	89	89	88.9
	558	71	89	89	88.5
	1032	71	89	90	88
ZnO/Kasil 1	0	79	92	93.5	93
	180	79	92	93	92
	558	79	92	93	92
	1032	79	92	93.5	93

The subsequent data (at 500 and 1000 ESH) reflect a stabilization of the organic coatings.

The relatively good properties and performance exhibited by S-13G Pigment/ Merck 261 in CREF Test No. 19 is repeated in this test. The S-13G Pigment/Dow ECR-34 coating performed similarly. In general, all of the coatings in Test No. 21 possess acceptable initial properties and reasonable stability.

3.4 Remarks on Environmental Test Results

The coatings tested all have conductivity values considerably higher than that of S-13G/LO. Most also have reasonable low α_s values. While we can be reasonably assured of the optical stability of these coatings, their electrical property stability remains in doubt. We have not calculated α_s for these materials because most are highly d elopmental. The tests consequently were designed to provide comparative information rather than absolute values. It is important to stress that we have measured only optical properties in-situ, not electrical properties. We do not know whether the latter arise from intrinsic photoconductive or extrinsic processes, or combinations of them. In overview, the coating tests and the environmental stability tests have served to identify several promising pigment/binder systems.

4. CONCLUSIONS

The objectives of this program were to evaluate materials approaches to solving the spacecraft SCA problem—basically, to assess various approaches toward the development of space-stable, electrically conductive, low α_s/ϵ spacecraft thermal control coatings. Emphasis was placed on conductive paint binders, primarily because, in classical paint coatings, the binder is the continuous (homogeneous) phase and the pigment is the dispersed phase.

From an overall point of view, the inorganic silicate coatings offer the greatest potential toward solving the SCA problem. Z-93 in particular, a NASA specification coating system, holds the greatest promise for an immediate, yet practical ("off-the-shelf") solution. Within 1 to 2 years, we could expect that a superior inorganic coating could be developed. Historically, however, the use of inorganic coatings for spacecraft temperature control has been limited, – primarily because of the belief that such coatings are difficult to apply and to keep clean.

The reluctance to accept inorganic coatings makes it imperative that organic coatings for anti-SCA use be developed. Because of our experience with the binder wetting problem, we believe that there are only two basic approaches. The first is the modification of specification (that is, flight qualified) coatings; the second, the

development of new coatings. The modification approach could involve, in increasing order of potential benefit, simple additives, structural changes to the polymeric binder, copolymerization, chemical complexing, and conductive pigments. We have assigned this order because we have not been able to find any electrically conductive additive compatible with RTV602 and because a conductive pigment (at high PVC) in RTV602 has markedly improved conductivity (compared to RTV602). The difficulties associated with obtaining effective structural changes either by complexing or copolymerization or otherwise are judged to be intermediate.

The development of new anti-SCA coatings represents a monumental task because of all the other principal requirements that space-stable low α_s/ϵ coatings must meet. Here too there are two basic approaches. The first is through the modification of current electrically conductive polymers; the second, through the development of new polymers.

Of considerable importance in all of the above conclusions and observations are the criteria for evaluating acceptable properties and performance of anti-SCA coatings. We are concerned that the lack of any correlations of electrical conductivity with anti-SCA performance detracts seriously from the relevance of most measurements of electrical properties. It may not even be proper to claim that materials with low surface or bulk resistivity are better anti-SCA materials than those with high values, unless, for instance, the resistivity vs applied electrical stress characteristics are known and accounted for.

In summary, the results of this program indicate that inorganic coatings are viable materials for both immediate and near term practical anti-SCA materials. Organic coatings will require substantial investments in time and funds. The necessity to meet conventional requirements for space-stable low σ_s/ϵ materials assures a long developmental period.

Acknowledgments

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