

The effect of the space environment on thermal control coatings

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ABSTRACT

The optical characteristics of spacecraft surfaces are fundamental parameters in controlling its temperature. Passive thermal control coatings with designed solar absorptance and infrared emittance properties have been developed for various space conditions and environments. In this total environment, the coatings must be stable and maintain their desired optical and mechanical properties for the course of a particular mission ranging up to a lifetime of thirty years.

This paper reviews stable polymeric and inorganic materials which we have developed for different orbital missions, both near earth and geosynchronous. Physical characteristics of these coatings such as hardness, flexibility, and out-gassing behavior are presented. The response of optical properties as a function of conditions such as ultraviolet-vacuum and atomic oxygen and also the function of time are discussed.

1. INTRODUCTION

In the early days of spacecraft materials' development, ultraviolet (UV) irradiation in vacuum testing was the principal means for evaluating optical stability. Additionally, the contributions of high energy electron and proton radiation, micrometeoroids and space debris, system-generated contamination and atomic oxygen (AO), were also recognized and addressed. The particularly degrading effects of AO have been observed from experiments on the Space Shuttle¹ and most recently from the Long Duration Exposure Facility (LDEF).

Our studies to develop spacecraft thermal control coatings for different missions have been directed primarily toward optical stability in this severe environment. In addition, our focus has been on coating systems which can be applied on relatively large surfaces under ambient conditions and also cured at room temperature. Maintaining the simplicity of the processing procedure was considered an important factor in obtaining desired materials reproducibility in optical and mechanical properties.

2. RESULTS AND DISCUSSION

2.1 Pigment screening

The early studies consisted of ultraviolet-vacuum screening tests for a large number of white powders as potential solar reflector pigments.² These tests were performed so that the less stable materials could be eliminated rapidly from any

extended study. Although much of this early work was performed prior to in situ reflectance measurements, the work is germane to the extent that: (1) pigments and materials shown to degrade by post-exposure measurements performed in air have been shown to never have degraded less when the measurements were subsequently performed in situ in vacuum; and (2) generally only the semiconductor pigments have been found to be very sensitive to oxygen bleaching, and the data on the many dielectric pigments examined were largely useful, though generally disappointing.

The results of UV-vacuum tests for selected pigments presented in Table 1 show that considerable coloration occurred in most of the pigments. Representative reflectance values are given for two wavelengths in the visible spectrum, 440 and 600 m μ . For most of the early screening work, reflectance curves in the visible spectrum were sufficient to suggest or preclude additional study.

In general, natural, mined minerals were less affected by UV irradiation in vacuum than synthetic laboratory chemicals. Exceptions were zinc compounds and tin oxide. For example, natural wollastonite was superior to synthetic calcium silicate. A marked difference in stability was apparent among different crystal forms of the same material. Metastable gamma alumina and cubic (unstabilized) zirconia degraded much more severely than their stable counterparts, alpha alumina and monoclinic zirconia. Purity in itself was not correlatable with stability. It was shown for Al₂O₃ and ZrO₂ that a 99% purity powder could be more stable than 99.9% material. Stability to a UV-vacuum environment is the result of a number of different factors in addition to purity (particle size and shape, surface chemistry, ionic activity, thermal history).

The early studies showed zinc oxide to be the most stable pigment; subsequent work revealed the stability of the mixed oxide, Zn₂TiO₄, to be equal to that of ZnO.^{3,4} The need for chemical treatment of these pigments to ensure stability is discussed in a later section.

2.2 Binder studies

Early inorganic binder candidates were monoaluminum dihydrogen phosphates, colloidal silica and various alkali silicates.¹ In UV-vacuum tests of formulations involving zirconia as the pigment, the silicate systems exhibited the smallest change in solar absorptance after 200 ESH:

	$\Delta\alpha_s$
Sodium silicate	0.04
Potassium silicate	0.06
Colloidal silica	0.14
AlH ₂ phosphate	0.11

The superior physical properties of silicate coatings compared to the soft silica formulations, along with room temperature curability compared to the 450°F needed for phosphates, made silicate binders the choice for extended studies.

Table 1. Effect of UV irradiation in vacuum on optical properties of miscellaneous inorganic pigments

Material	Manufacturer's Designation	Exposure ESH	Reflectance, %	
			440 μm	600 μm
Al_2O_3	Alucer MC (alpha)	0	100.0	100.0
		180	74.0	91.5
Al_2O_3	Alucer MA (gamma)	0	93.5	90.0
		75	49.5	82.5
Sb_2O_3	--	0	92.5	96.5
		75	36.5	50.0
BaCO_3	Reagent grade	0	98.5	99.0
		200	71.0	93.5
BN	HC 0021	0	88.5	92.5
		75	65.0	84.0
CaF_2	Reagent grade	0	94.5	97.0
		200	61.0	87.5
CaSiO_3	Synthetic	0	86.0	90.0
		75	58.0	81.0
CaSiO_3	Wollastonite C-1	0	92.5	94.5
		75	81.0	91.5
MgAl_2O_4	Spinel	0	97.5	97.0
		75	70.0	92.5
MgO	Reagent-grade powder	0	98.5	98.5
		75	71.0	92.5
SiO_2	Diatomaceous earth, Dicalite WB-5	0	92.0	93.5
		180	87.5	93.0
SiO_2	No. 7900 Vycor	0	94.0	95.0
		200	43.0	44.5
SnO_2	CP	0	88.0	90.0
		300	78.5	88.0
ZrO_2	CP (Monoclinic)	0	96.0	97.5
		75	75.5	92.5
ZrO_2	Cubic	0	88.0	95.5
		180	33.0	73.5
ZrSiO_4	Superpax	0	86.5	92.5
		180	65.0	84.5
ZnS	Reagent grade	0	91.0	94.5
		75	89.0	94.0
ZnO	SP 500	0	95.0	99.0
		75	95.0	99.0

Screening of organic coating binders involved commercially available silicones, fluorine-containing aliphatic resins, and modified silicone-epoxy compositions. Table 2 shows the effect of UV irradiation in vacuum of several organic coatings. The superior resistance of methyl silicone resins was observed in these studies, and the study of experimental methyl silicone resins comprised a major portion of early investigations.

Table 2. Effect of UV irradiation in vacuum on optical properties of several organic coatings pigmented with SP 500 ZnO

Resin Binder	Exposure ESH	Reflectance, %	
		440 μm	600 μm
Teflon FEP 120/COP* of tetrafluoroethylene and hexafluoropropylene	0	84.2	77.3
	314	52.4	67.5
Viton A/COP of vinylidene fluoride and hexafluoropropylene	0	88.0	94.0
	108	68.0	87.5
Kel-F 800/COP of vinylidene fluoride and trifluorochloroethylene	0	84.0	77.5
	108	64.5	72.5
Kynar L-18/polyvinylidene fluoride	0	84.0	90.0
	108	64.0	81.0
Exon 461/COP of vinyl chloride and trifluorochloroethylene	0	85.0	80.5
	108	10.0	31.5
Leonite 201-S/silicone-epoxy modified acrylic	0	86.0	85.0
	108	71.0	83.0
806A/methyl phenyl silicone	0	89.0	87.5
	108	56.0	83.5
RTV-11/methyl silicone	0	91.0	92.0
	500	88.0	91.5
LTV-602/methyl silicone	0	91.0	93.5
	500	90.0	93.5

*Co-polymer

2.3 Coatings development

All coating formulations contain three ingredients: pigment, binder, and enough diluent to achieve a sprayable consistency. The pigment-to-binder ratio (PBR) is maximized to achieve the highest reflectance attainable and to maximize UV-vacuum stability. The binder component is responsible for lower reflectance in the infrared, and also is more susceptible to optical damage. The maximum pigment loading is governed by desired physical properties, i.e., if a harder inorganic surface is required, higher binder concentration is used. With silicone coatings, composition is dictated by the degree of elastomeric behavior and of specularly desired.

Coatings which have been developed at IITRI are shown in Table 3, along with some of their properties. All of the coatings are applied by spray techniques and cured at room temperature. In general, excellent adhesion is achieved on metal surfaces such as aluminum or magnesium when appropriate substrate preparation is taken. This can be mechanical abrasion to obtain higher surface area for improved bonding, or when such surface treatment cannot be tolerated, appropriate primers or coupling agents are used. Cleanliness is an extremely important consideration in the processing of coatings, both from the standpoint of good initial physical properties and of good optical stability in a space environment.

TABLE 3. Solar reflectors: physical properties

	Z93	S13G/LO-1	YB-71 (ZOT)
Composition	ZnO-potassium silicate	ZnO (encapsulated) - methyl silicone	Zn ₂ TiO ₄ -potassium silicate
Pigment-Binder Ratio	4.3:1	2.0:1	7.1:1
Application	Spray/RT	Spray/RT	Spray/RT
Handling	24 hours	4 hours	24 hours
Cure	7 days	7 days	14 days
Physical Behavior	Slightly flexible, hard surface	Very flexible, soft surface	Slightly flexible, very hard surface
Cleanability	Protection Required	Yes	Protection Required

The S13G/LO-1 is a fourth generation material,⁵ reflecting evolutionary changes in testing, material requirements, and material availability. The original S13 consisted of a ZnO pigment (SP500/New Jersey Zinc) in a polydimethylsiloxane (RTV 602/GE). Evaluation of S13 using in situ measurements reveals a reflectance decrease of about 35% at 2000 nm (2 μ) after approximately 800 equivalent sun hours (ESH) of UV irradiation in vacuum (Figure 1). However, an essentially instantaneous increase in infrared reflectance occurs when either air or oxygen is admitted to the irradiated specimen; the recovery is very nearly total after only two minutes of exposure to air (Figure 1).

The effect of 1000 ESH of UV radiation on a pigment specimen of SP500 ZnO is shown in Figure 2. These data show that the bulk of the solar absorptance increase exhibited by ZnO as a powder, and as a paint in the S13 coating, is due to the oxygen-bleachable damage sustained in the infrared.

The rapidity that the UV-induced infrared absorption band develops in ZnO and the abruptness with which oxygen annihilates the absorption strongly indicates that the infrared phenomenon is not related to bulk diffusion phenomena but is associated with the photodesorption of absorbed oxygen. IITRI's Z93 thermal control coating, an SP500 ZnO-pigmented potassium silicate paint, did not undergo the bleachable infrared damage exhibited by S13 and pure ZnO. Figure 3 is a typical spectra of irradiated and unirradiated Z93, which is seen to be quite stable to UV radiation in vacuum.

2.3.1 S13G

The absence of damage to ZnO-pigmented alkali silicate coatings suggested that the reaction of ZnO with the potassium silicate may have precluded the bleachable infrared degradation exhibited by ZnO powder and ZnO-pigmented silicone paints. The polydimethylsiloxanes do not "wet" the pigment particles and consequently it was conjectured that they do not offer an effective barrier to photodesorption reactions on the surface of ZnO. A series of experiments were performed in which ZnO was first reacted with potassium silicate and then extracted and dried as a new, treated ZnO pigment. It was shown that a ZnO powder treated (reactively encapsulated) in this way does not exhibit infrared degradation. The reflectance spectra of an irradiated silicate-treated ZnO specimen are presented in Figure 4.

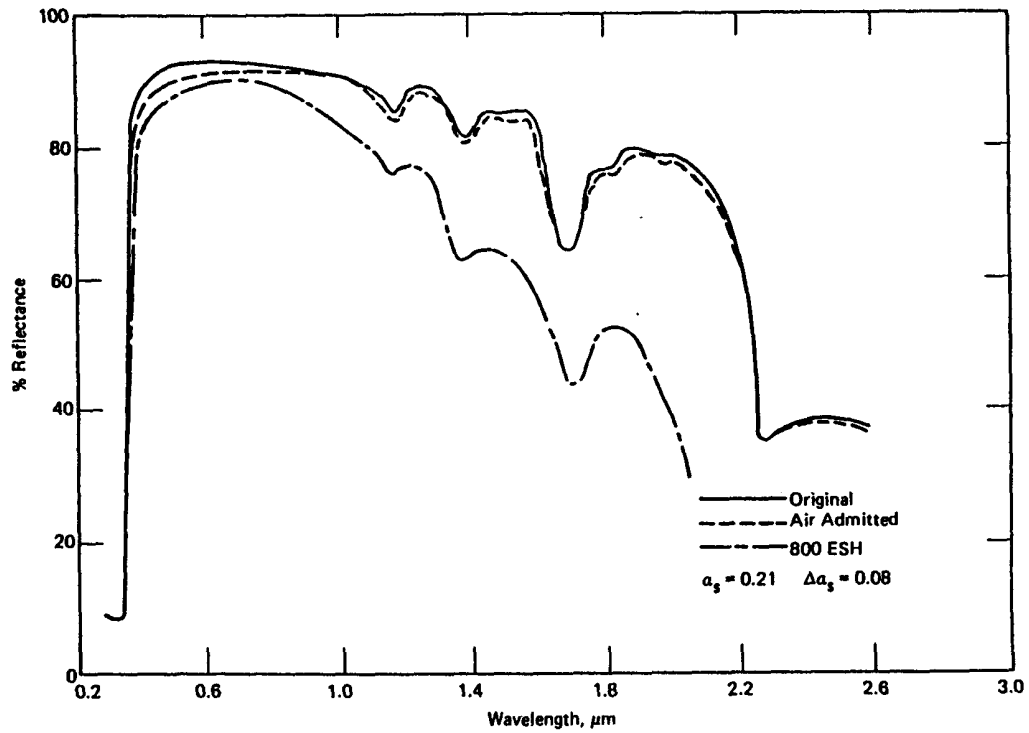


Figure 1. UV Degradation of S-13.

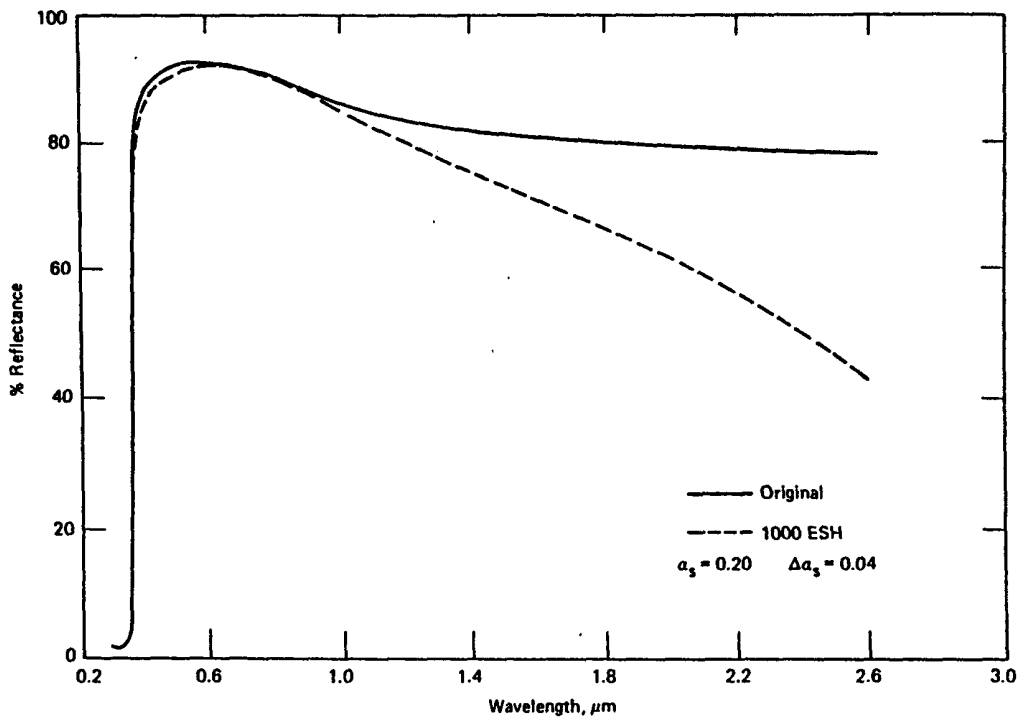


Figure 2. UV Degradation of ZnO.

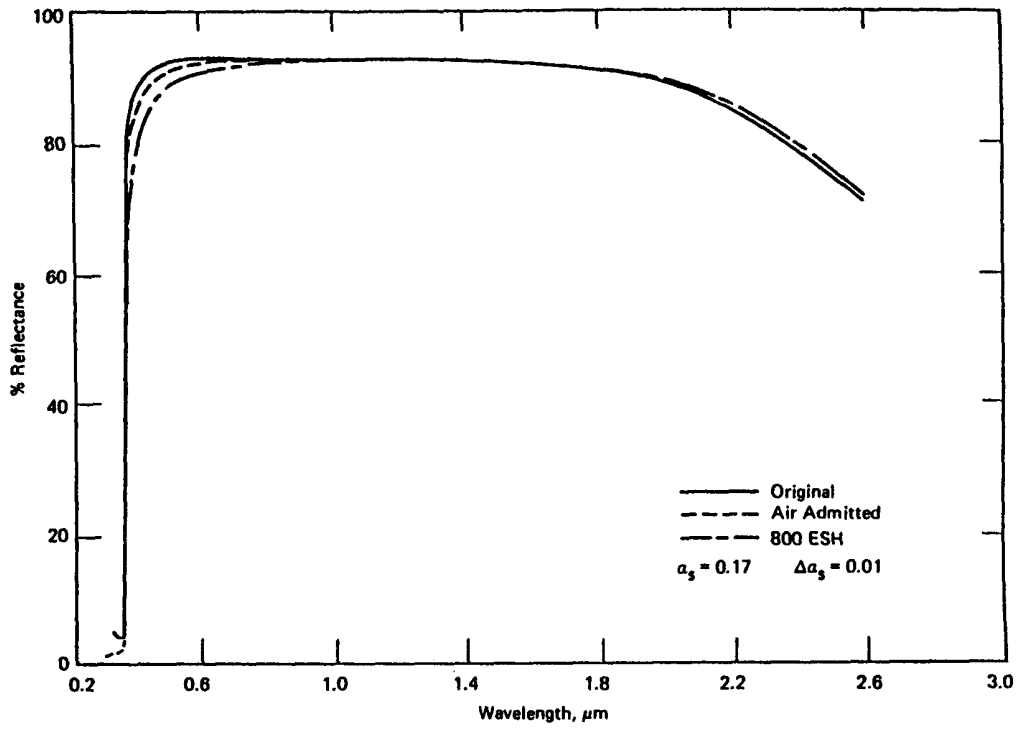


Figure 3. UV Degradation of Z93.

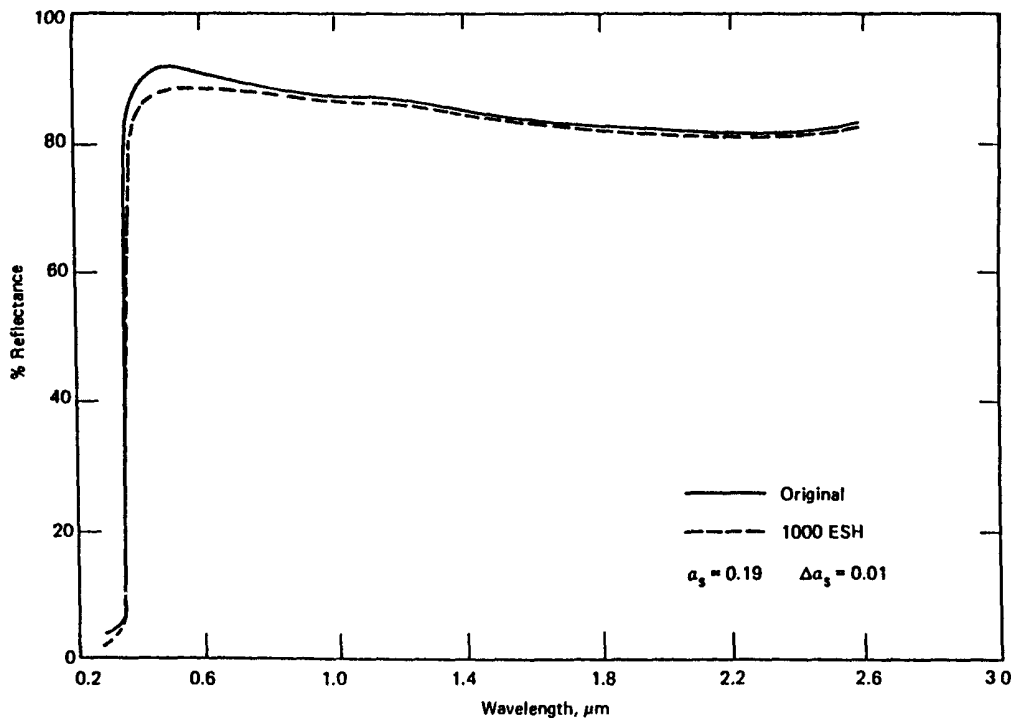


Figure 4. UV Degradation of silicate-treated ZnO.

2.3.2 S13G/L0

The deleterious effect of outgassing, i.e., volatilization of degradable components from spacecraft surfaces which would condense on critical areas such as optics, was recognized in the early 70's. Criteria were established by NASA for an outgassing test involving exposure of the test material for 24 hours to 125°C at a pressure of less than 10^{-6} torr. The sample is weighed before and after the test to determine total weight loss (TWL). The volatile condensable material (VCM) is determined from the amount of material condensing on a collector plate maintained at 25°C.

It was determined that the standard production batch S13G was marginal in meeting the 1.0% TWL and 0.1% VCM. Studies were conducted to develop improved stripping procedures for the RTV 602. Molecular distillation to remove low molecular weight components was found to be an effective means of obtaining the desired minimal outgassing characteristics. The result of these studies was S13G/L0.

2.3.3 S13G/L0-1

The removal of RTV 602 silicone from the marketplace in the early 80's necessitated development of yet another S13 material to take its place. Studies were conducted with the objective of developing a clone so that users of S13G/L0 would have available a material which would not seriously affect or change design criteria. The data in Figure 5 show that the current generation S13G/L0-1 is somewhat more reflective and slightly more stable than its predecessor.

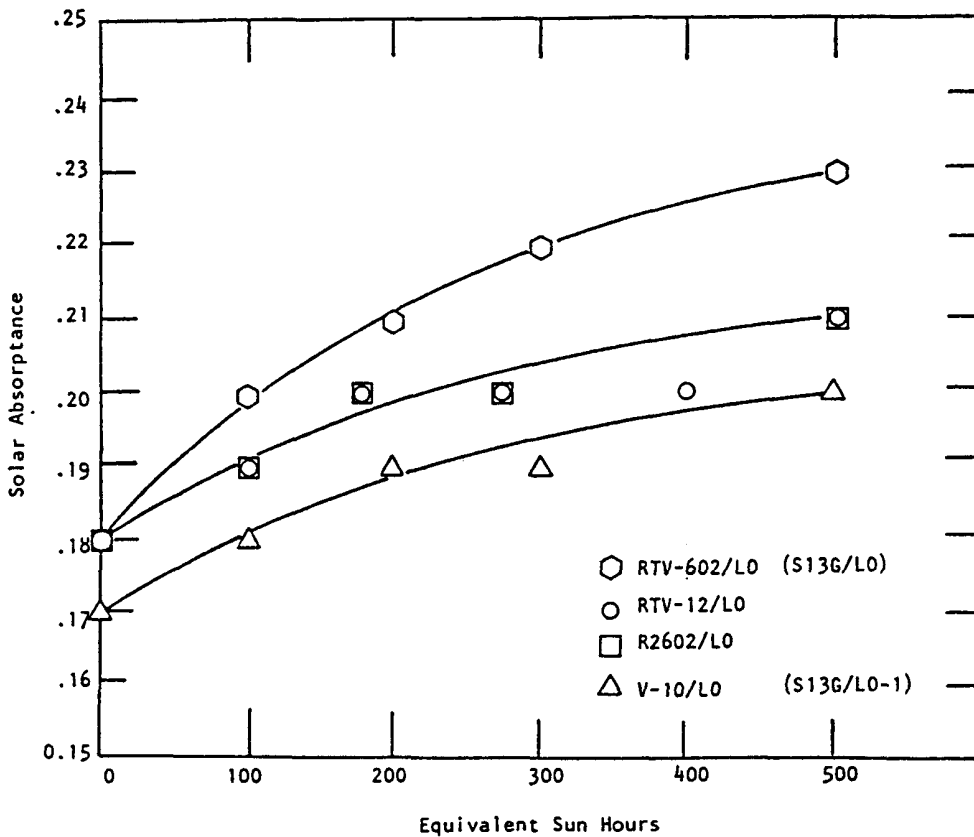


Figure 5. Solar absorbance vs. equivalent sun hours for different resin systems.

2.4 Space environment effects

In considering the characteristics of the coatings listed in Table 3, it is apparent that the particular mission demands will determine which system should be used. For near-earth orbital flights of relatively short duration or for use on thin, flexible substrates, a silicone system such as IITRI's S13G/LO-1 has been used extensively. For missions of longer periods and where stability to particulate radiation as well as UV is crucial, inorganic systems have been specified.

The optical properties and the response of our solar reflector coatings to space environmental factors are presented in Table 4. A 5000 ESH test conducted at NASA/Marshall Space Flight Center has been our most extended laboratory test on these coatings. The results for this test presented in Table 5 reveal a change in solar absorptance of about 0.02 for the YB-71 samples. In the same test, Z93 exhibited a $\Delta\alpha_s$ of about 0.03, and S13G/LO a change of 0.06. In all cases, emittance was not affected by UV-vacuum.

Table 4. Solar reflectors: thermo-optical properties

	Z93	S13G/LO-1	YB-71 (ZOT)
Composition	ZnO-potassium silicate	ZnO (encapsulated) - methyl silicone	Zn ₂ TiO ₄ -potassium silicate
Solar Absorptance	0.15	0.18	0.10
Total Normal Emittance	0.90	0.90	0.90
$\Delta\alpha_s$, 5000 ESH	0.03	0.10	0.02
Thermal Shock Resistance	Good	Good	Good
Atomic Oxygen Resistance	Good	Good	Good
Outgassing: TML	1.5%	0.2%	1.5%
VCM	0	0.02%	0
Temperature Capability	700°C	300°C	900°C

Table 5. Changes in solar absorptance and emittance after 5000 ESH exposure

Sample	Solar Absorptance, α_s			Emittance, ϵ_{TN}	
	Initial	After 5000 ESH	$\Delta\alpha_s$	Initial	After 5000 ESH
YB-71 (1112)	.149	.166	.017	.907	.905
YB-71 (185)	.131	.151	.020	.885	.884
YB-71 (205)	.155	.166	.011	.893	.890
YB-71 (190A)	.174	.193	.019	.896	.894
YB-71 (LH112)	.122	.145	.023	.890	.888
Z93	.174	.202	.028	.896	.895
S13G/LO	.184	.245	.061	.901	.900

Long-term data for YB-71 has been generated in a geosynchronous orbit (GEO) flight experiment.⁶ Solar absorptance data determined from calorimetric measurements for the ZOT coatings on aluminum revealed the following optical behavior:

Days After Launch	α_s	$\Delta\alpha_s$
0	0.19	
400	0.26	0.07
800	0.30	0.11
1200	0.31	0.12
1600	0.32	0.13

In comparison, much stronger degradation of $\Delta\alpha_s = 0.26$ has been observed for S13G/LO from NAVSTAR 6 after about 3 years in GEO. Current technology indicates an initial α_s of ≤ 0.12 for YB-71. Based on comparable rates of solar absorptance degradation observed for different ZOT samples, a lower terminal α_s of ≤ 0.25 may be anticipated after an extended period in GEO.

Low earth orbit (LEO) altitudes are considered to lie within the range of 200 to 600 km. At these altitudes, the major atmospheric constituent is atomic oxygen (AO) which occurs as a result of UV dissociation of molecular oxygen, and which attacks a variety of materials through both oxidation and erosion processes. Coatings have been flown on short term shuttle flights, and S13G/LO and YB-71 have been shown to be resistant to AO, exhibiting no change in α_s or ϵ . A compilation of AO effects on materials was reported by Banks et al⁸ at a recent NASA/SDIO workshop. The data for YB-71 and S13G/LO were as follows:

Coating	Erosion Yield, $\times 10^{-24}$ cm ³ /atom	$\Delta\alpha_s$	$\Delta\epsilon$
YB-71	0.0	0.005	0.0
S13G/LO	0.0	-0.005	0.0

The compositional makeup of the silicate and silicone materials is such that oxygen needs are satisfied, obviating any oxidation effects.

Contamination, both molecular and particulate, has caused degradation in both optical and thermal control systems. Outgassing tests based on ASTM E-595-77 have been conducted on the three IITRI coatings by Ball Aerospace and McChan Nusil. The results for TML (total mass loss) and VCM (volatile condensable material) have been on the average 0.2% TML and 0.02% VCM for S13G/LO-1 which are well within the NASA criteria of 1.0%/0.1%. No VCM is observed for the water-based inorganic coatings, even though the TML is above 1%. This small amount of water would be purged away quickly by the vacuum of space, and the inorganic coatings can be considered non-outgassing for the long-term mission requirements.

2.5 Preliminary results from LDEF experiments

The recent recovery of the Long Duration Exposure Facility (LDEF) and its experimental packages have enhanced our knowledge of the long-term performance of materials and systems in the natural and induced space environment. The LDEF mission provided over 5½ years of space exposure for its 57 experiments. The Thermal Control Surfaces Experiment (TCSE) was the most complex experiment on the LDEF and was designed to study the effects of the space environment on thermal control surfaces. The TCSE combined in-space spectral reflectance measurements of test materials with extensive pre- and post-flight analyses to study these effects. The post-flight analysis of the TCSE is underway and detailed results will be available later this year.

Some observations can be made from the detailed LDEF/TCSE inspections and initial post-flight thermo-optical measurements of the TCSE samples. The individual effects as well as the combined effects of the atomic oxygen, solar UV, thermal vacuum, micrometeoroid/debris, and contamination are apparent on the LDEF and TCSE surfaces. Some surfaces showed discoloration due to contamination and solar UV exposure while others showed a lack of expected discoloration, apparently due to the scrubbing effect of atomic oxygen. The texturing and erosion effects of the ambient atomic oxygen is apparent on polymeric materials such as FEP Teflon.

The TCSE flight sample array included three IITRI white coatings--S13G/LO, Z93, and YB-71. The S13G/LO white paint did degrade, as expected, in the almost six year space exposure. However, this degradation of the solar absorptance was significantly greater than was predicted from ground simulation testing. The inorganic coatings, Z93 and YB-71, were very stable for the LDEF/TCSE mission with almost no change in thermo-optical properties.

The preliminary LDEF/TCSE results show that there are white coatings which are stable in the low earth orbit space environment. The available materials are limited and new materials and coatings will be required to meet the challenges for future space missions. Experiments like the LDEF and the TCSE must continue to be flown to better characterize the performance of current and new materials for different environments and mission durations.

3. SUMMARY

Both the polymeric (S13G/LO-1) and inorganic (Z93 and YB-71) coatings show good resistance to the UV and charged particle radiation, atomic oxygen, and vacuum-induced behavior to be encountered in space. However, other hostile threats such as micrometeoroid hits, plasmas, electrical discharge, laser and nuclear effects can all seriously compromise the survivability of these spacecraft materials. There is a continuing need for new, more stable materials for longer missions in the complex, hostile space environment.

4. REFERENCES

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