THE PERFORMANCE OF THERMAL CONTROL COATINGS ON LDEF AND IMPLICATIONS TO FUTURE SPACECRAFT

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SUMMARY

The stability of thermal control coatings over the lifetime of a satellite or space platform is crucial to the success of the mission. With increasing size, complexity, and duration of future missions, the stability of these materials becomes even more important. The Long Duration Exposure Facility (LDEF) offered an excellent testbed to study the stability and interaction of thermal control coatings in the low-Earth orbit (LEO) space environment. Several experiments on LDEF exposed thermal control coatings to the space environment. This paper provides an overview of the different materials flown and their stability during the extended LDEF mission. The exposure conditions, exposure environment, and measurements of materials properties (both in-space and postflight) are described. The relevance of the results and the implications to the design and operation of future space vehicles are also discussed.

INTRODUCTION

With the exception of the limited experimentation conducted aboard *Skylab*, LDEF has provided the only retrievable space exposure opportunity to test the long-term performance of thermal control coatings. Subsequent sample evaluation and data analysis has provided a wealth of information that is now being made available to aid in the design of future spacecraft. As an example of this, Space Station *Freedom* (S.S. *Freedom*) will employ the thermal control coating Z-93 extensively on large and complex structures. This is due in large part to the confidence generated by the stability Z-93 demonstrated on the LDEF mission.

This paper discusses the thermal control coatings tested on LDEF and the available data concerning the performance of these thermal control coatings on the LDEF mission. In addition, the implications for future spacecraft are discussed. It should be emphasized that the results presented here are not final and that in most cases analyses are continuing. Much of the data are not fully understood or explainable at this time.

Many of the 57 LDEF experiments exposed thermal control coatings to the LDEF environment either as test specimens or as operational coatings. In addition, several coatings were used as thermal control surfaces on LDEF itself. When the available data on these materials are evaluated along with the preparation, exposure, and measurement conditions, there will be several factors that complicate this analysis. In many cases there were no ground and/or flight control samples to establish a measurement baseline or to determine the effects of aging alone on these materials. Where there were control samples, many were either not stored under controlled conditions or were lost over the unanticipated 5-year delay in the recovery of LDEF. This long and uncertain mission duration also resulted in lost or incomplete preflight data and documentation. In addition, some test samples were prepared using different techniques, procedures, material batches, and sample thicknesses.

One of the most significant problems in comparing the different LDEF data on coatings is the difference in measurement instruments. Investigators used a number of different instruments that are difficult to compare. In many cases, the instruments used for preflight measurements have been replaced with new instruments or they have been upgraded or modified. Even with these complications, the LDEF experiments provide the most extensive data base on the performance of thermal control coatings in the space environment.

The available thermal control coatings data from the LDEF experiments and from the LDEF system have been reviewed. Data from selected experiments and samples have been analyzed and compared to compile this paper. Tables 1 and 2 list the experiments, their location on LDEF, and the coatings that are considered in this paper.

Table 1. Selected LDEF experiments with thermal control coatings.

Experiment No.	Ref. No.	LDEF Row	Title	PI	Organization
S0069	1,2,3 4	9	Thermal Control Surfaces Experiment	Wilkes Zwiener	AZ Technology NASA/MSFC
A0171	5	8	Solar Array Materials Passive LDEF Exposure (SAMPLE)	Whitaker	NASA/MSFC
A0114	2	3,9	Interaction of Atomic Oxygen with Solid Surfaces at Orbital Altitudes	Gregory Peters	Univ. of AL-HSV NASA/MSFC
M0003-5	6	3,9	Thermal Control Materials	Hurley	UDRI
M0003	7	3,4,8,9	DOD Materials Experiment	Jaggers Meshishnek	Aerospace Corp.
A0138-6	8	3	FRECOPA	Guillaumon Paillous	CERT
LDEF Components	9 10 11	----	LDEF Materials SIG Analysis	Golden Pippen Bourassa	The Boeing Co.
S1003	12	6	Ion Beam Textured and Coated Surfaces Experiment	Mirtich Rutledge	NASA/LeRC
S1001 A0076	13	1,9	Low Temperature Heat Pipe Experiment and Cascade Variable Conductance Heat Pipe Experiment	Kauder	NASA/GSFC

Table 2. Selected LDEF experiments with thermal control coatings.

Experiment Coating	S0069 (TCSE)	A0114 (UAH)	A0171 (SAMPLE)	S1003 (IBEX)	GSFC (Kauder)	M0003-5 (Dayton)	M0003 (Aerospace)	A0138-6 (FRECOPA)	MSIG
Z-93	X	X				X		X(6)	
S13G/LO	X	X	X	X	X	X	X	X(6)	X
A276	X	X	X			X	X	X	X
YB-71	X					X	X		
D111	X					X	X		
Z302	X	X	X			X		X	
Z306	X	X	X			X		X(7)	X
Chromic Acid Anodize	X					X			X
RTV 670/A276	X								
OI650/A276	X								

Notes for Table 2.

1. 401-C10 (Nextel) black, Z853 yellow, Tiodize K17 black, Tiodize K17 white
2. 401-C10 (Nextel) black, black chrome
3. SiO_x over Kapton™; 200, 500, 700, 1,000 Å
4. Acrylic/Urethane over Kapton™; silicone over Kapton™, RTV 615 white paint
5. NS43G; white silicone Eu 203 MeSi, a Al 203 MeSi, PV100, TiO_2 MeSi, DC 92-007
6. White paints similar to S13G and Z-93:
   PY100, 536, PSB, SG11, FD, PSG 120 FD, and conductive white paints PCB-2, PCB-T, PCB 119
7. Black paints similar to Z306:
   PU1, Cuvertin 306, VHT SP102, HT 650, Electrodag 501, L300, PNC, PUC.

The exposure environment for the test samples varied with the row location of the experiment on LDEF. Figure 1 shows the exposure environment by row number on LDEF (refs. 1,2).

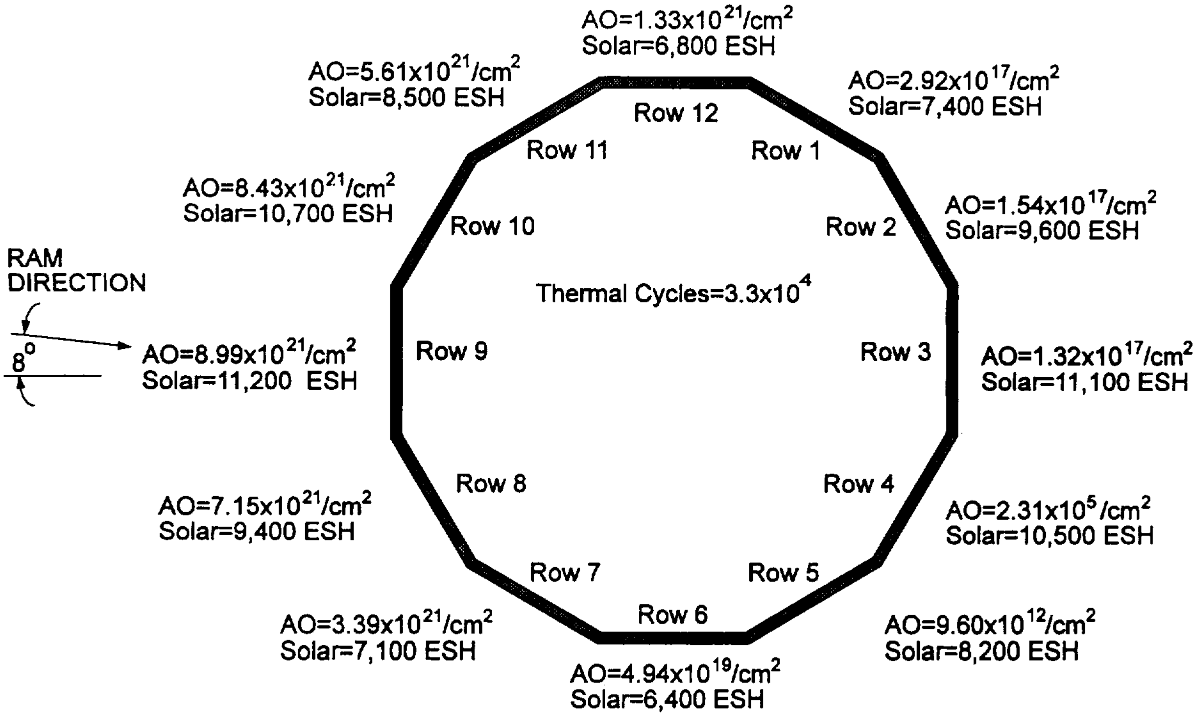

Figure 1. LDEF exposure environment.

The extended LDEF exposure caused significant changes in many coatings. These include optical as well as other surface physical changes. Surface changes include:

- The surfaces of silicones exposed to the RAM atomic oxygen were converted to SiO_x components and suffered microscopic cracking (ref. 3).
- There were trace contaminants on most LDEF surfaces (refs. 4–6):
  - Hydrocarbon contaminants were not present on RAM facing surfaces
  - Silicone contaminants were present in trace amounts on most surfaces
  - The effects of trace level contaminants were not significant for most thermal control coating applications.
- There was localized heavy contamination with significant optical degradation near contaminant sources and vents.
- The UV fluorescence of some coatings were changed (ref. 7).
- AO protective coatings suffered cracking, crazing, and peeling (ref. 8).
- Urethane and epoxy based coatings erode readily in AO (ref. 8).

OPTICAL EFFECTS

The material properties of a coating that are of the greatest concern are solar absorptance (α_s) and thermal emittance (ε_t). α_s and ε_t directly affect the thermal control of a spacecraft. The ε_t for all the materials presented here were basically unchanged by the LDEF exposure (ref. 8). Spectral reflectance measurements are the best method to determine α_s and provide the materials engineer with insight into the optical signature and stability of a material as a function of exposure environment and duration. Data are presented for a number of the more widely used and accepted thermal control coatings, illustrating the change in solar absorptance of these materials for the extended LDEF mission. Because of the difference in the stability of these materials, please note the scale change of the abscissa on graphs for different materials.

Z-93 Ceramic Nonspecular White Coating

The renewed interest in the white thermal control coating Z-93 (manufactured by the IIT Research Institute) is because it has been shown to be highly stable in the LEO environment. The results from LDEF, and in particular the Thermal Control Surfaces Experiment (TCSE-S0069), have demonstrated this stability through the in-flight optical data that are not subject to the uncertainties of data generated from pre- and postflight sample measurements alone. In addition to the LDEF demonstrated stability of Z-93 in LEO, it can be deposited onto large, complex structures with relative ease and with low weight and cost per square area. As a result of these characteristics, Z-93 has been baselined for use on the radiators and some of the antennas which will compose the critical and intricate structure of S.S. *Freedom*.

In Figures 2 and 3, Z-93 data from several experiments are plotted, both on the LDEF's leading and trailing edges. Change in solar absorptance is plotted against exposure time. The unique in-space optical measurements performed on experiment TCSE-S0069 provide a time history of changes in α_s. These in-space measurements also allowed investigations to develop a trend analysis and a prediction model for the material and to better understand the damage mechanisms affecting its optical stability (ref. 9). The data from the Z-93 samples indicate that it was very stable over the LDEF mission, and data from three experiments corroborate these findings for both leading and trailing edge samples. The trend analysis studies also provide some insight into the small changes that were measured.

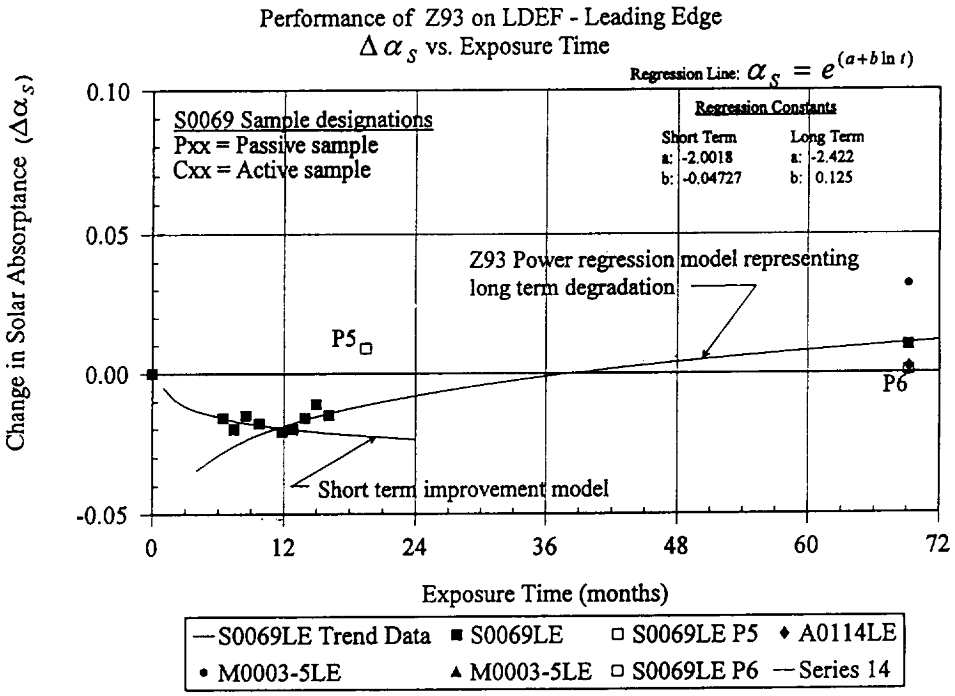

Figure 2. Performance of Z-93 on LDEF—leading edge.

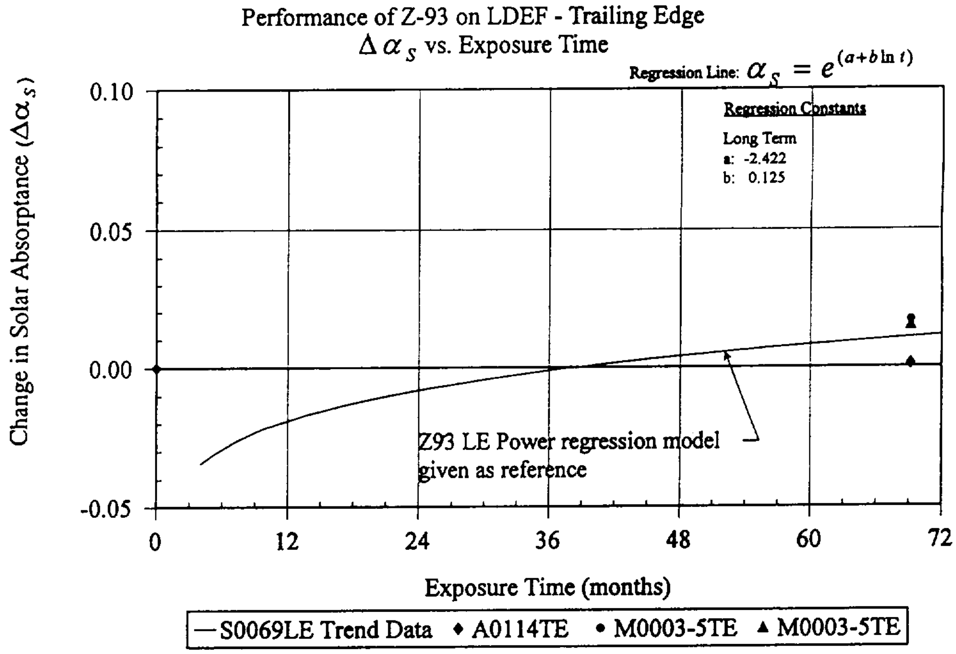

Figure 3. Performance of Z-93 on LDEF—trailing edge.

There appear to be at least two mechanisms affecting the Z-93 solar absorptance for the LDEF mission. The first is an improvement (decrease) in α_s typical of silicate coatings in thermal vacuum. This improvement is normally associated with loss of interstitial water from the ceramic matrix. Ground laboratory simulation tests have shown this process takes a much shorter time than the TCSE flight data suggests. This slower loss of water may be due to the cold temperature of the TCSE Z-93 sample mounted on a thermally isolated calorimeter. The temperature of the Z-93 sample ranged from approximately –55 °C to +6 °C but remained well below 0 °C most of the time. The short-term improvement is dominant for the first year of exposure after which a long term degradation becomes dominant.

This trend analysis is being expanded to include the TCSE spectral reflectance data shown in Figure 4, and to analyze how Z-93 changed at specific wavelengths. The increase in infrared reflectance early in the mission results in the improvement in α_s, while the decrease at shorter wavelengths is the long term degradation component for Z-93. This trend analysis is providing an analytical prediction model for specific materials and offering insight into the degradation mechanisms of Z-93. These data generated from the TCSE demonstrate the value of in-space optical measurements on materials.

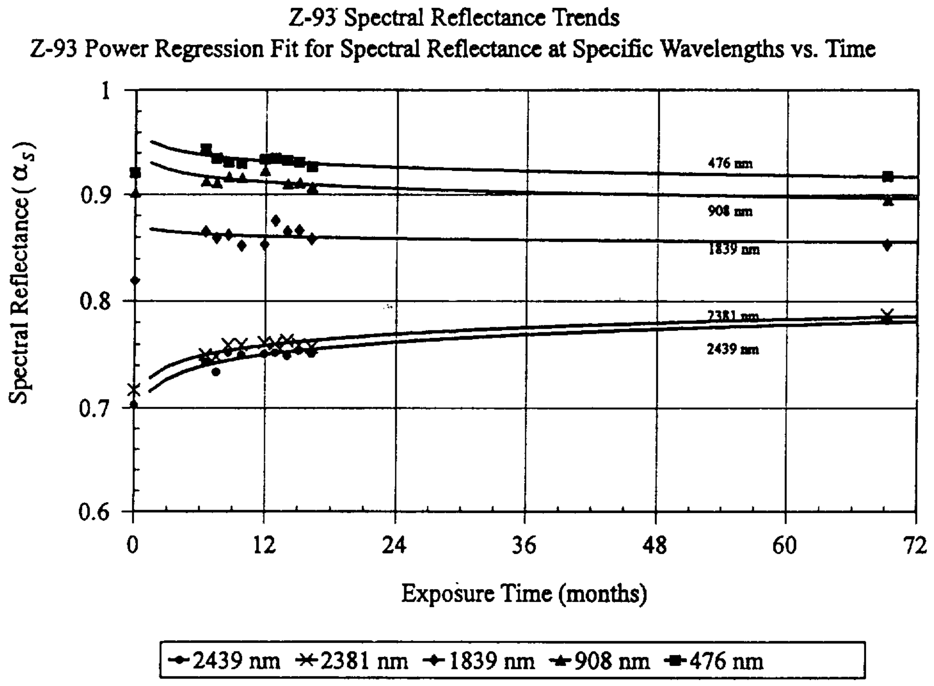

Figure 4. Z-93 spectral reflectance trends.

Z-93 IR Spectra

In Figure 5, the infrared spectra for both the exposed and unexposed areas of the Z-93 coating on flight sample C3-41 are plotted. The spectra was generated using a Fourier scanning infrared attenuated total reflectance microprobe system (SPECTRA TECH IRμs/SIRM system, technical assistance provided by Drs. J.A. Reffner and P.A. Martoglio). The system configuration used to analyze this sample has a beam spot area of approximately 53 microns. The shift in the silica absorption band maximum from 1,019 to 1,026 cm^{-1} and the extinction of the 1378 cm^{-1} absorption band of the exposed Z-93 are thought to be accurate at this time. The trend to a general slight increase in reflectance of the exposed area of this sample may be caused from changes in its surface morphology rather than a chemical change. These changes to the samples surface may have affected the light scattering characteristics of the material resulting in the observed change in the IR reflectance. These are preliminary results and will require further investigation to determine their validity. However, it is thought that this is the first time such data and associated exposure effects have been reported for this spacecraft thermal control coating as such.

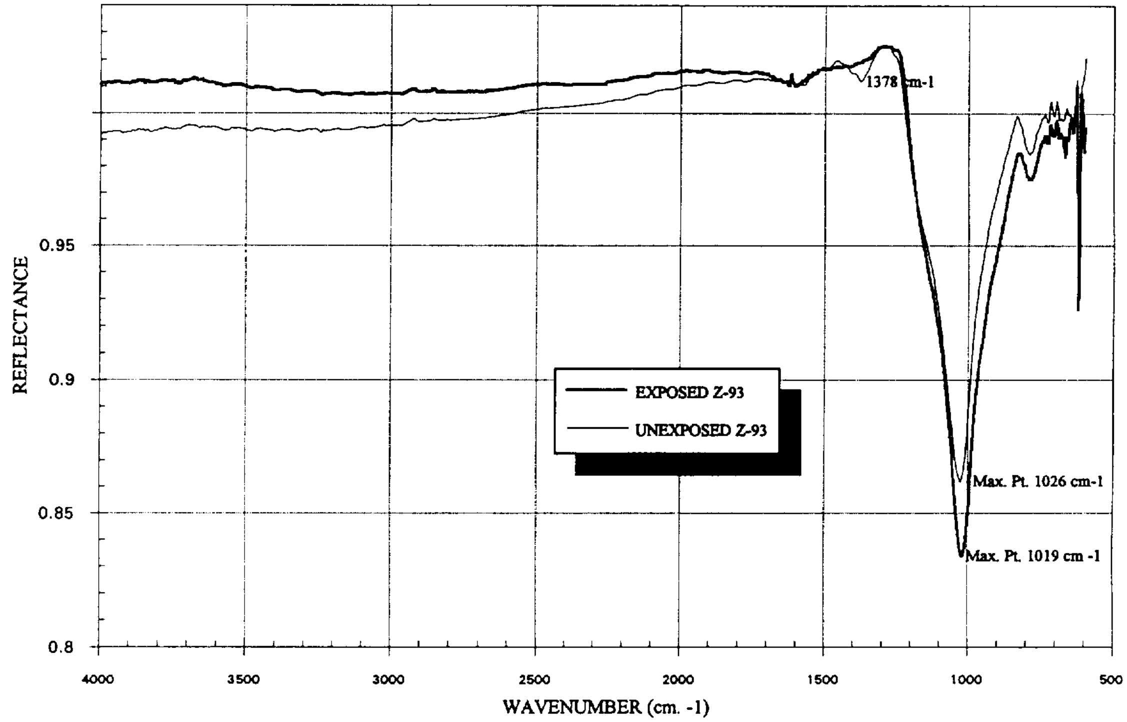

Figure 5. Exposed and unexposed Z-93 thermal control coating, sample C3-41, mode, microscopic attenuated total reflectance.

YB-71 and YB-71/Z-93 Ceramic Nonspecular White Coating

The YB-71 (manufactured by IIT Research Institute) coatings behaved similarly to the Z-93 samples. A small increase in the infrared reflectance early in the mission caused a decrease in α_s (Figures 6 and 7). This was offset by a slow long-term degradation resulting in a small overall increase in α_s. The samples with YB-71 applied over a primer coat of Z-93 had a somewhat lower initial α_s than the other YB-71 samples. YB-71 samples were flown on two experiments—the TCSE (S0069) and M0003. The TCSE samples were consistently more stable than the M0003 samples. The YB-71 samples were prepared for LDEF before the development of YB-71 was finalized. These differences could be due to batch variations of this new coating. There was no significant difference in the performance of leading and trailing edge samples on M0003. The M0003-5 YB-71 showed a slightly higher $\Delta\alpha_s$ than those samples on TCSE. The power regression model is shown for the TCSE data.

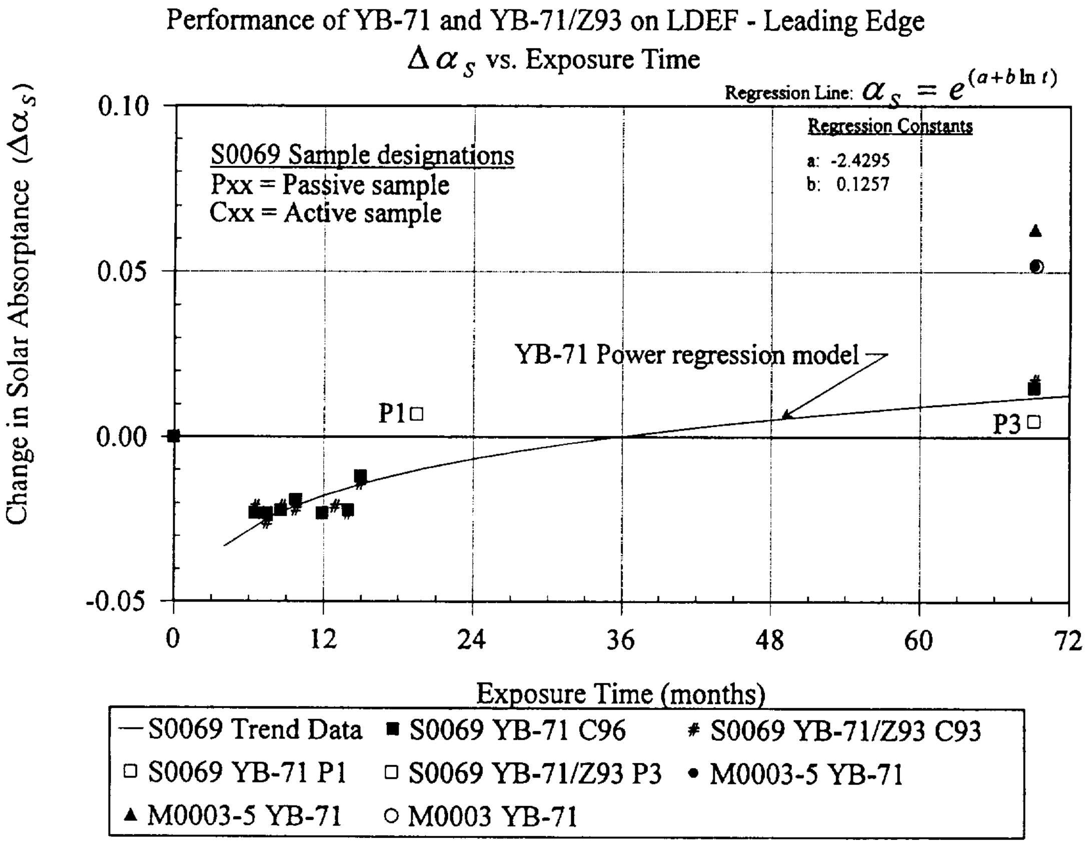

Figure 6. Performance of YB-71 and YB-71/Z-93 on LDEF—leading edge.

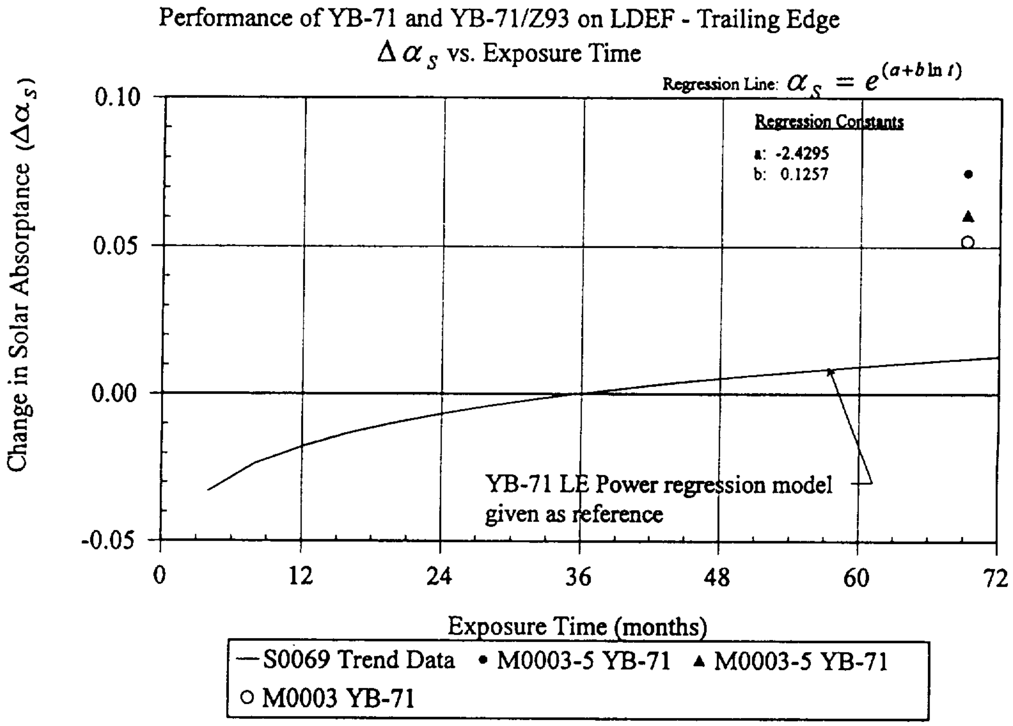

Figure 7. Performance of YB-71 and YB-71/Z-93 on LDEF—trailing edge.

S13G/LO Silicone Nonspecular White Coating

There is a wide variation in the results from the different LDEF experiments for S13G/LO (manufactured by the IIT Research Institute). These differences are unexplained at this time. Figures 8 and 9 show the change in α_s for the LDEF mission of several S13G/LO samples. There does not appear to be any clear correlation between ram and wake locations with respect to degradation in α_s of S13G/LO. The S0069 power regression model is shown and falls in the middle of the spread of data reported for the various experiments.

The interaction of the space environment with S13G/LO is very complex. However, from what is presently known about the LDEF environment and this type of material, material changes are likely to be the result of several factors or synergistic interactions. Some of components in this interaction which need to be considered are vacuum ultraviolet (VUV), ultraviolet (UV), atomic oxygen (AO), contamination, and material batch variability. The VUV, UV, and AO can combine to cause reaction (conversion) and ionization of the coating. This results in chain and aliphatic group scission and crosslinking of the polymer binder. Ultimately AO reaction with the silicone polymer causes glassification and trapping of residual carbon to produce color centers. The production of color centers is not only dependent on incident radiation and AO reaction, but also on material batch processing characteristics and contamination. Synergistics of these factors can exaggerate the observed change in solar absorptance of this and similar types of materials.

A276 White Specular Polyurethane Paint

The A276 (manufactured by Lord Chemical Co.) coating provides an excellent example of the synergistic effects of solar UV and AO impingement (Figures 10 and 11). Apparently, the oxidation and subsequent loss of the polyurethane binder prevented significant buildup of damaged material. When protected from AO the damaged, intact surface material and contaminants resulted in large increases in α_s. On LDEF, the majority of AO exposure occurred in the latter few months of the mission. This AO exposure may have eroded away the slight amount of degraded surfaces seen on the S0069 samples (ram) during the first part of the mission.

RTV670 and OI650 Silicone Overcoats on A276

An attempt was made to protect the A276 coating from AO erosion with overcoats of silicone. In Figure 10, the S0069 results of RTV670 (manufactured by General Electric, no longer being produced) and OI650 (manufactured by Owens Illinois, Television Products Division) over A276 are shown. The overcoat prevented material loss but allowed, presumably, solar UV damage of the A276 coating and possibly damage and darkening of the silicone protective layer. In addition, the silicone layer was cracked due to AO glassification and this may have resulted in shrinkage and loss of mass. Further investigations are ongoing to resolve these questions. There were no samples of the silicone coatings alone flown on LDEF.

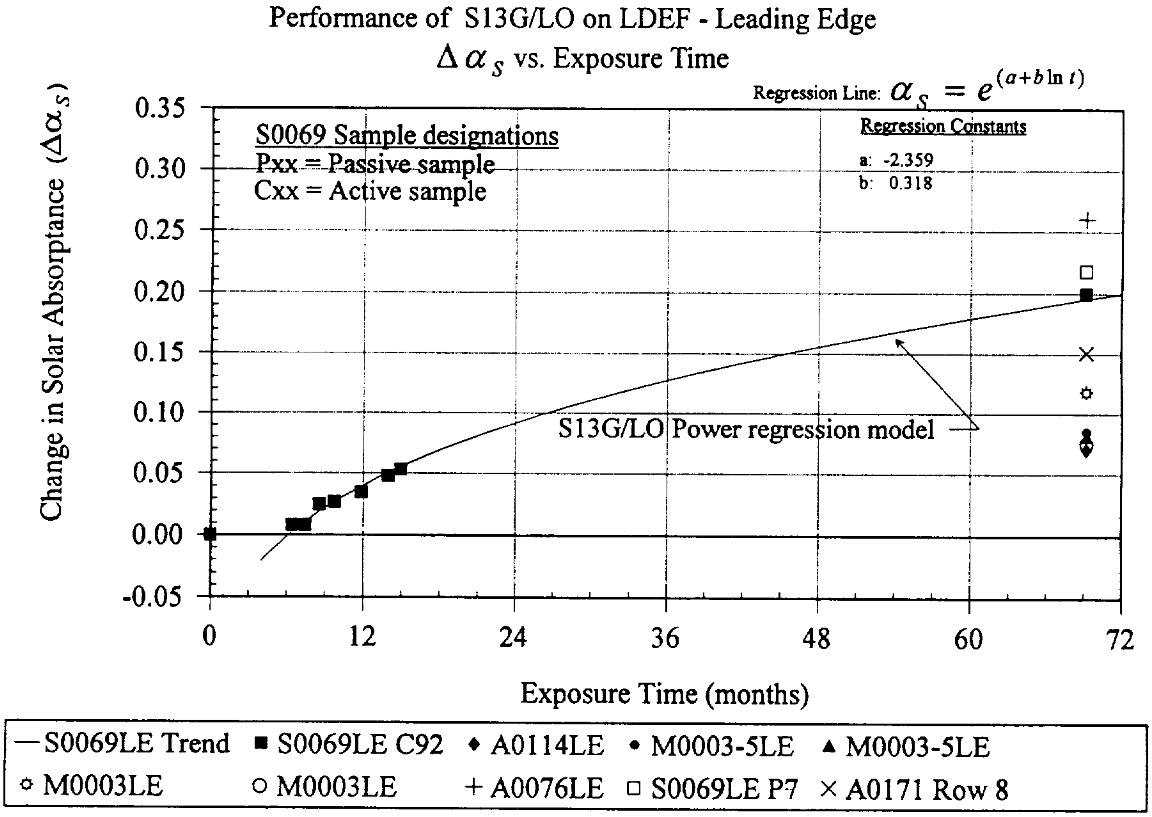

Figure 8. Performance of S13G/LO on LDEF—leading edge.

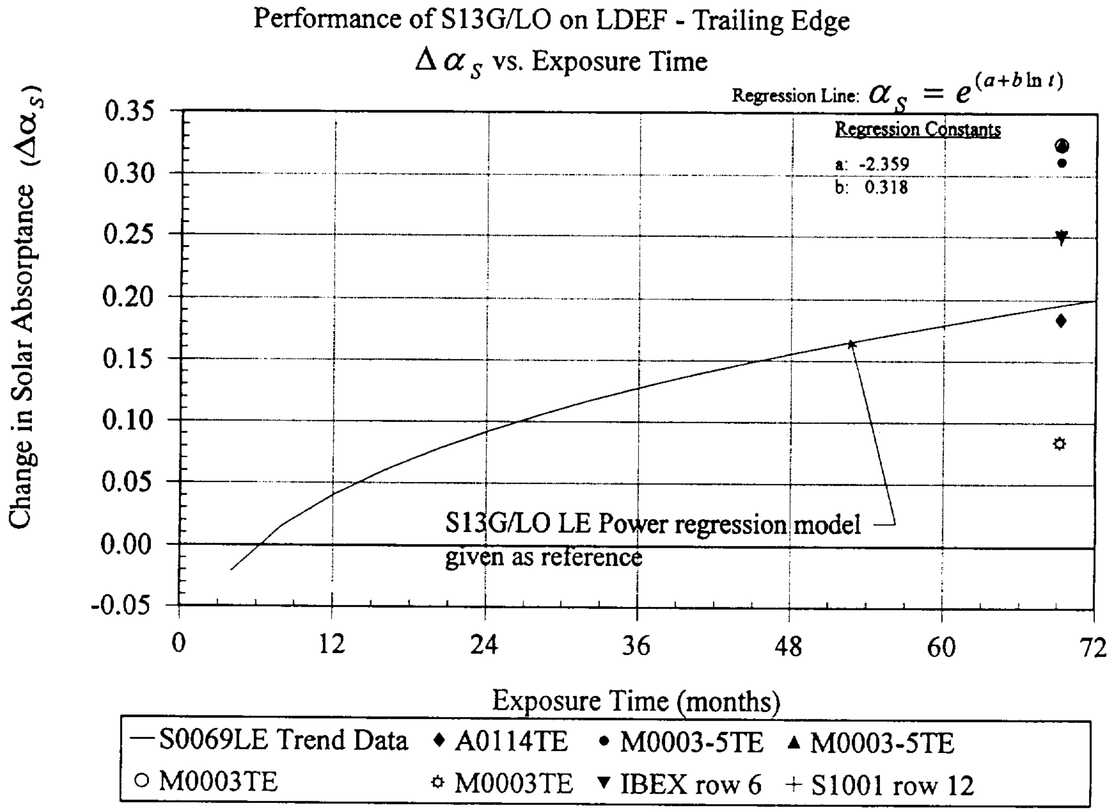

Figure 9. Performance of S13G/LO on LDEF—trailing edge.

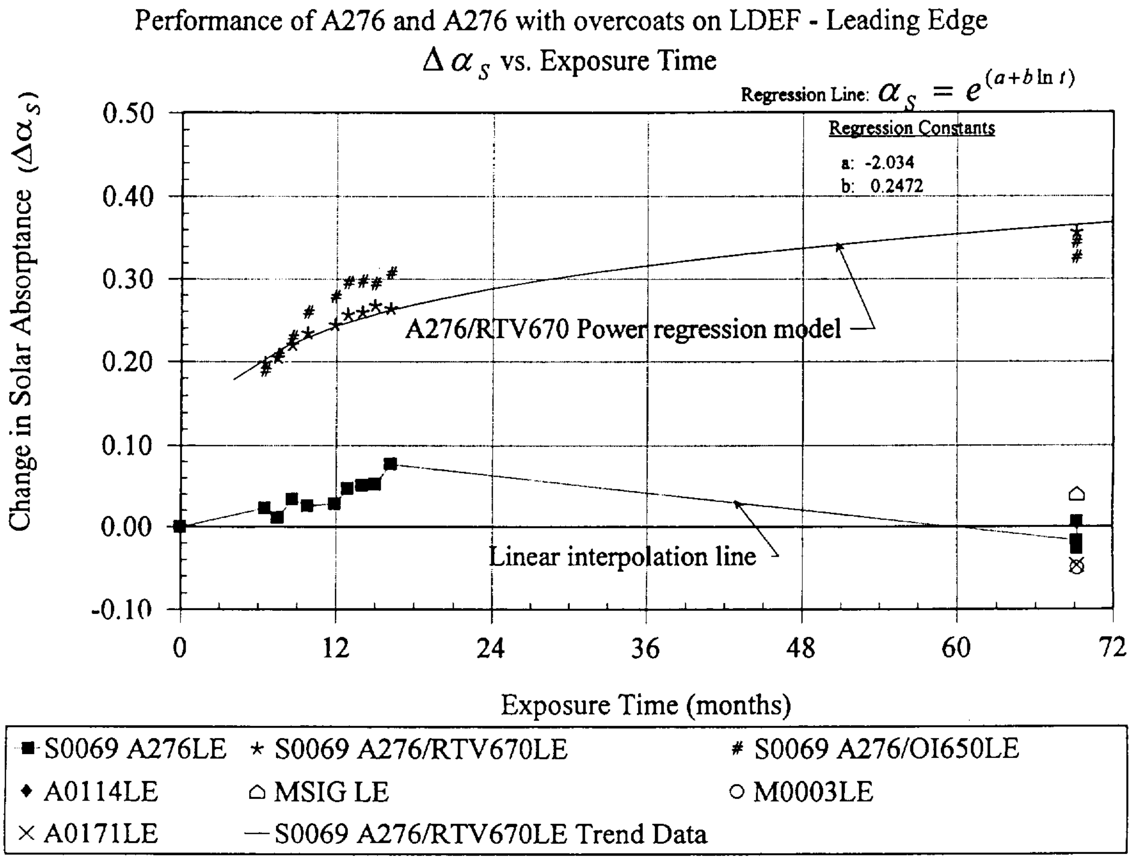

Figure 10. Performance of A276 and A206 with overcoats on LDEF—leading edge.

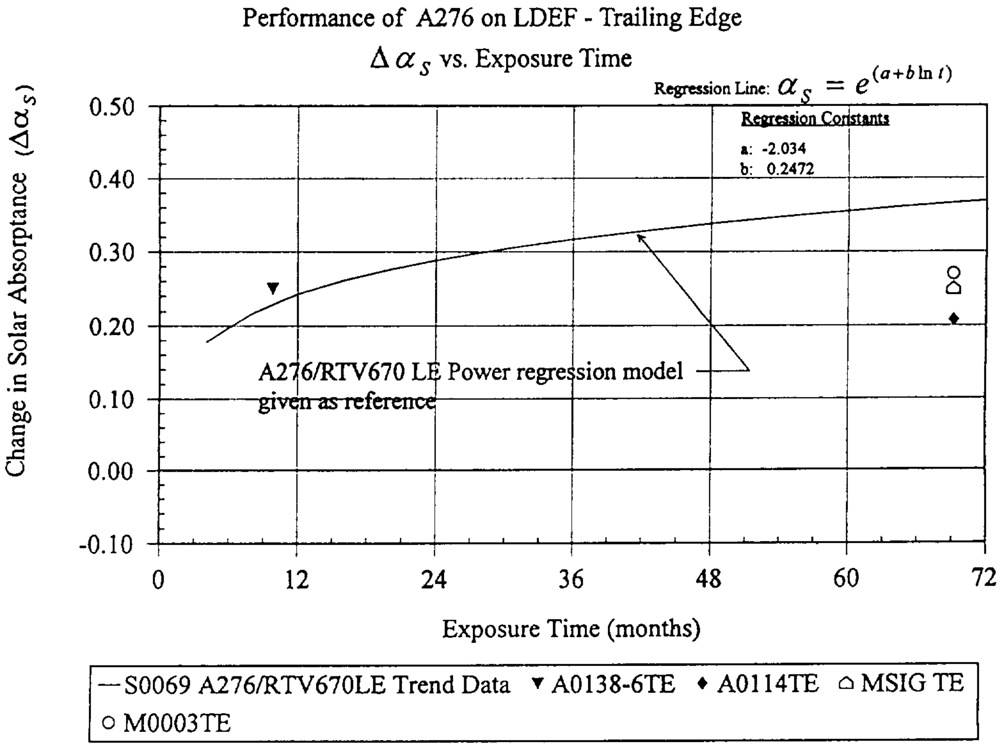

Figure 11. Performance of A276 on LDEF—trailing edge.

CHEMGLAZE Z302™ and Z306™ Polyurethane Black Paints

Z302 and Z306 (manufactured by Lord Chemical Company) are polyurethane-based gloss and flat black paints, respectively. They have been shown to be susceptible to AO interactions that result in erosion of the polyurethane binder and their carbon pigment when not protected from AO effectively. Several of the samples of Z302 exposed on the S0069 experiment (TCSE) had protective overcoats deposited onto their surfaces to evaluate the effectiveness of these materials. The samples with overcoats of either RTV670 or OI650 showed little change in solar absorptance (Figure 12). However, the surface of the silicone overcoatings have undergone some significant morphological changes. These changes are demonstrated primarily through the formation of fissures in the silicone likely resulting from the shrinkage of the overcoat material as it lost mass from AO, radiation, and general LEO space environmental exposure.

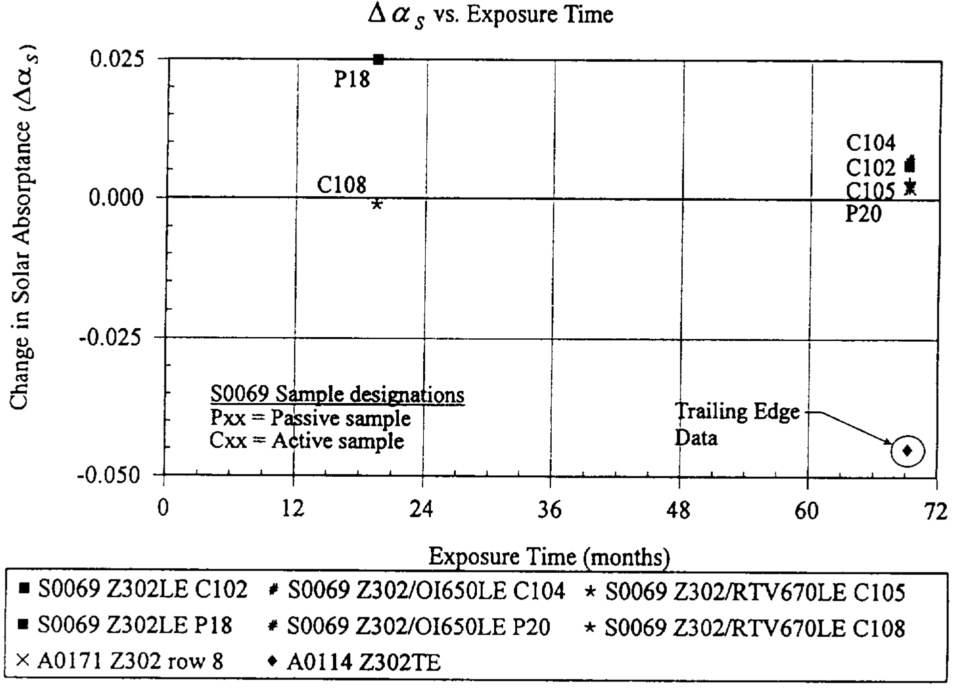

Figure 12. Performance of Z302 and Z302 with overcoats on LDEF—leading and trailing edge.

Visually these samples appear to have sustained no AO damage to the underlying polyurethane coating, but some mechanical damage has occurred. This damage is likely to have occurred as a result of the stresses that were developed in the laminated coatings as the silicone overcoat shrank and was exposed to the normal thermal cycling processes occurring on the experiment as it went in and out of solar exposure. As expected, unprotected Z302 was heavily eroded by the AO exposure. Two of the S0069 Z302 coatings were exposed to the environment for the total 5.8 years of the LDEF mission. These unprotected Z302 sample surfaces eroded down to the primer coat. Two other samples were exposed for only 19.5 months and, while they did erode somewhat, still possessed good solar absorptance (Figure 12). Uncoated samples of Z302 on A0114 showed considerable change (decrease) in α_s on the trailing edge sample, presumably due to a loss of material even with reduced AO exposure. The AO114 Z302 sample was completely eroded from the unprotected and uncovered area of the A0114 sample. Optically, Z306 was stable with the exception of an A0114 sample and an A0138-6 sample, both wake positioned, but showing $\Delta\alpha_s$ changes of about –0.04 (Figure 13). Physical and mechanical analysis of Z306 samples is planned for the future.

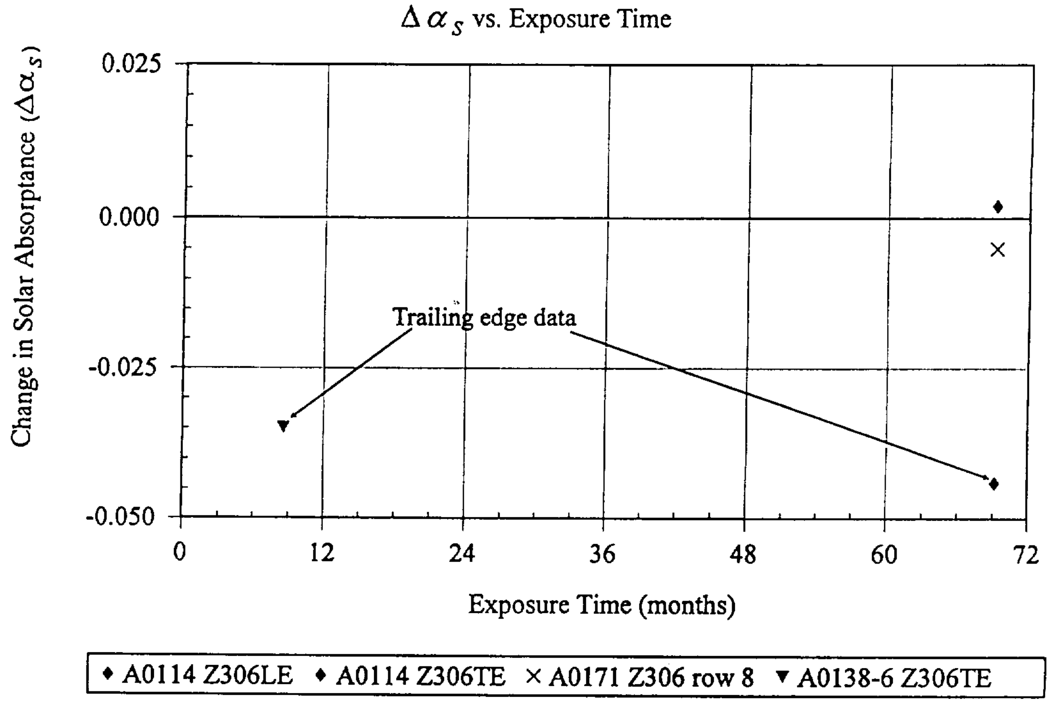

Figure 13. Performance of Z306 black paint on LDEF—leading and trailing edge.

D-111 Ceramic Nonspecular Black Coating

D-111 (manufactured by IIT Research Institute) black coating samples flown on LDEF demonstrated themselves to be relatively stable in LEO both in the ram and wake orientations (Figure 14). The D-111 coating was stable for both of these positions with the exception of the one M0003 trailing edge sample. This is curious since the pigment is a carbonous material and one may have expected some AO reaction with the pigment. However, it may be assumed that the glass binder effectively protected the pigment from AO interaction.

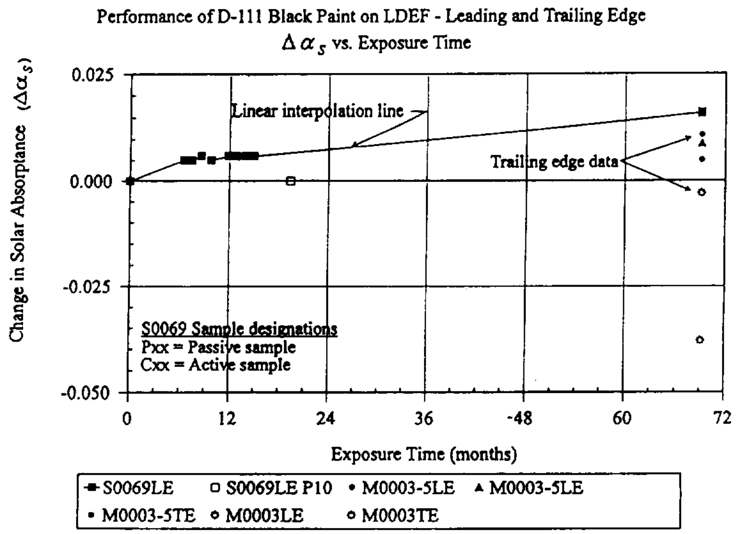

Figure 14. Performance of D-111 black paint on LDEF—leading and trailing edge.

IMPLICATIONS TO FUTURE SPACECRAFT

Spacecraft designers frequently need coatings with α_s and ε_t values tailored for a particular application. These requirements range from low α_s/high ε_t for many thermal radiator applications to many other combinations of low-to-high α_s and low-to-high ε_t. Figure 15 shows the range of coatings and films that can be prepared in the laboratory. However this range of available materials is more limited for space applications. Figure 16 shows that even though the selection is more limited there is still a wide range of coatings suitable for short-term applications. For long-term applications, this range of suitable materials is severely limited (Figure 17). The "LDEF test" validated only a few of these coatings for long-term applications. These include Z-93 and YB-71 white ceramic coatings, silver Teflon™ (when properly applied), thin chromic acid anodized aluminum and possibly D-111 black ceramic coating.

Because of the different combinations of space environment constituents, the range of coatings that are usable in geosynchronous earth orbit (GEO) are somewhat different than for LEO applications, but are also very limited (Figure 18).

With the limited range of proven coatings, designers of space hardware for long-term missions must accommodate the optical properties (α_s, ε_t) of these coatings. The behavior of coatings in the space environment is still not well understood, and conservative end-of-life estimates for coatings must be used. Until this materials/environment interaction is better understood and improved coatings are developed, the stability of coatings in the space environment will continue to be a limiting factor in the technology for long term missions.

CONCLUSION

The LDEF and its complement of experiments have provided unique data for the long-term effects of the space environment on thermal control materials. These data have already played a significant role in the selection of materials for S.S. *Freedom* and other space missions. While the "LDEF test" is currently the definitive data, there is significant spread in the data, and many questions remain about the synergistic effects of the space environment on materials. Additional flight experiments dedicated to materials effects are needed to better understand the response of materials to various environments. These experiments should include active experiments that perform optical and other measurements similar to those performed in ground laboratories. These experiments will provide the additional benefits for improved lifetime prediction models and better ground simulation testing. Many materials were badly degraded during the extended LDEF mission. Only a few thermal control coatings passed the "LDEF test." New materials are needed to broaden the range of stable coatings for long term applications.

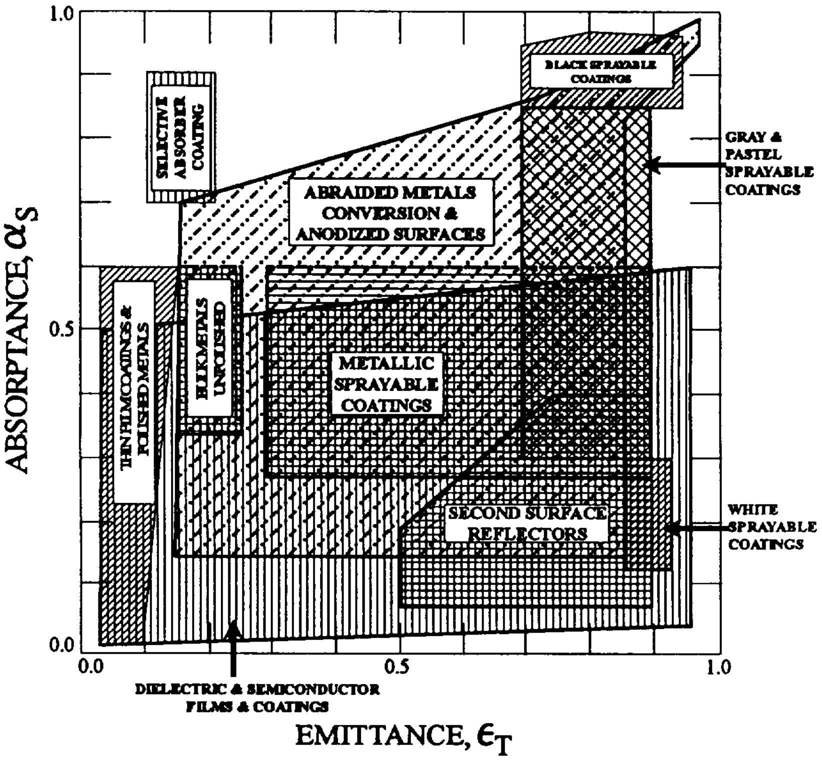

Figure 15. Available coatings and surfaces.

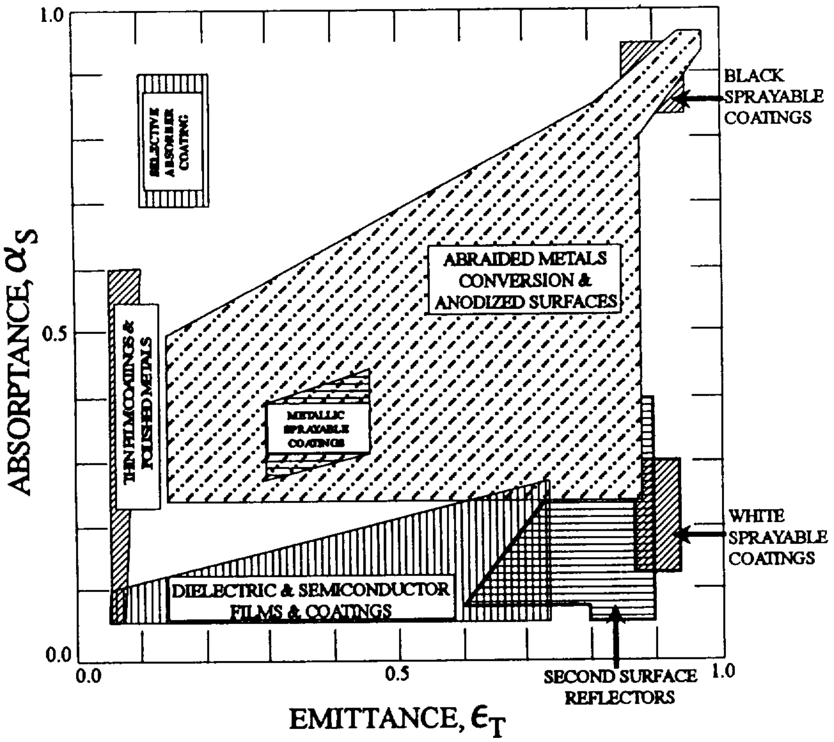

Figure 16. Usable coatings and surfaces—LEO short term.

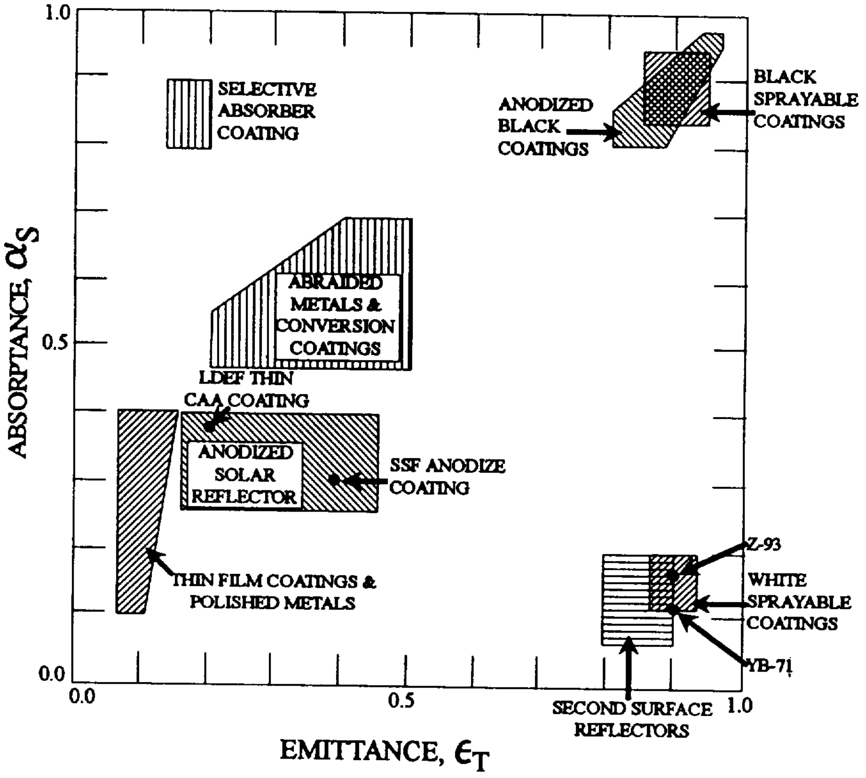

Figure 17. Usable coatings and surfaces—LEO >5 years.

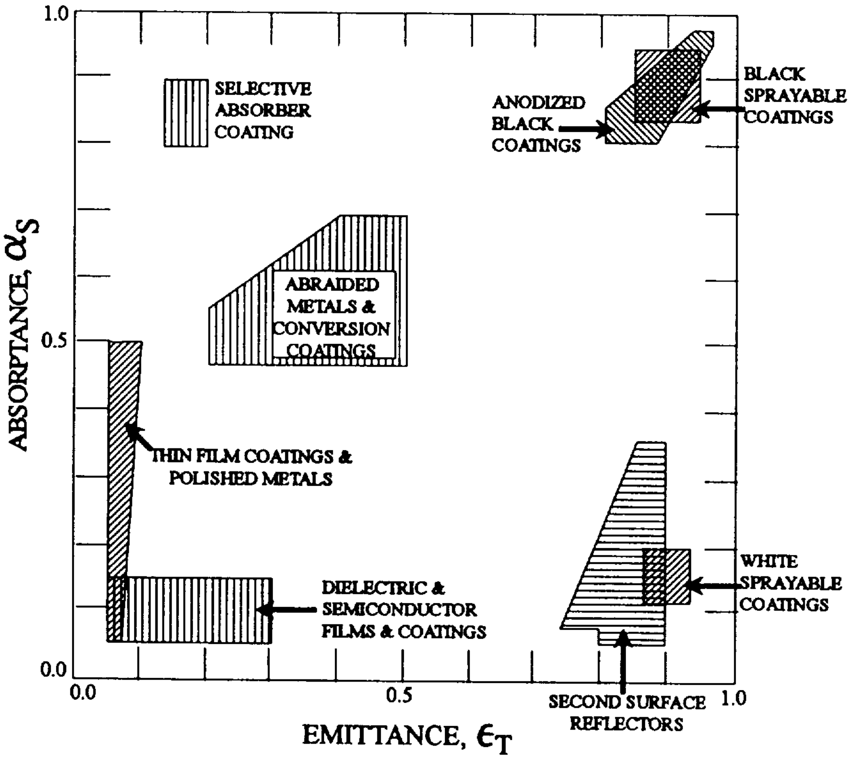

Figure 18. Usable coatings and surfaces—GEO 1 to 7 years.

REFERENCES

1. Bourassa, R.J., Gillis, J.R., and Rousslang, K.W.: "Atomic Oxygen and Ultraviolet Radiation Mission Total Exposures for LDEF Experiments." LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2-8, 1991, pp. 643–661.

2. "LDEF Atomic Oxygen Fluence Update." NASA Conference Publication 3162, November 1991, pp. 59–69.

3. Banks, B., et.al.: "Atomic Oxygen Interactions with FEP Teflon™ and Silicones on LDEF." LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 801–816.

4. Pippin, H.G., and Crutcher, E.R.: "Contamination on LDEF Sources: Destruction and History." LDEF—69 Months in Space, Second Post-Retrieval Symposium, June 1–5, 1992.

5. Crutcher, E.R., et.al.: "Molecular Films Associated with LDEF." LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 155–177.

6. Harvey, G.A., et.al.: "Sources and Transport of Silicone NVR." NASA Conference Publication 3162, November 1991, pp. 175–184.

7. Zwiener, J., et.al.: "Unusual Materials Effects Observed on the Thermal Control Surfaces Experiment (S0069)." LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 919–934.

8. Wilkes, D.R., et.al.: "Thermal Control Surfaces Experiment Initial Flight Data Analysis Final Report." Report No. 90-1-100-2, June 1991.

9. Wilkes, D.R., et.al.: "The Continuing Materials Analysis of the Thermal Control Surfaces Experiment." LDEF—69 Months in Space, Second Post-Retrieval Symposium, June 1–5, 1992.

BIBLIOGRAPHY

Golden, J.: “Selected Results for LDEF Thermal Control Coatings, M0003-8.” LDEF—69 Months in Space, Second Post-Retrieval Symposium, June 1–5, 1992.

Guillaumon, J.C., et.al.: “Spacecraft Thermal Control Coatings.” LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 945–960.

Hurley, C.J.: “Long Duration Exposure Facility Experiment M0003-5 Thermal Control Materials.” LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 961–974.

Jaggers, C., et.al.: “Thermal Control Paints on LDEF: Results of Sub-Experiment 802-18 M0003.” LDEF—69 Months in Space, Second Post-Retrieval Symposium, June 1–5, 1992.

Kauder, L.: “Preliminary Results for the LDEF/HEPP Thermal Control Samples.” LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 797–800.

Mirtich, M., et.al: “Ion Beam Textured and Coated Surfaces Experiment (IBEX).” LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 989–1004.

Pippin, H., et.al.: “Survey of Results from the Boeing Modules on the M0003 Experiment on LDEF.” LDEF—69 Months in Space, First Post-Retrieval Symposium, NASA CP3134, June 2–8, 1991, pp. 1109–1114.

Whitaker, A.: Solar Array Materials and Passive LDEF Exposure, AO171, NASA, MSFC, private communication.

Wilkes, D.R., et.al.: “Thermal Control Surfaces on the MSFC LDEF Experiments.” NASA Conference Publication 3162, November 1991, pp. 187–209.