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**Thermal Control Paints on LDEF:
Results of M0003 Sub-Experiment 18**

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Mark Borden John Kyle Smith

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Several thermal control paints were flown on LDEF, including the white paints Chemglaze A276, S13GLO, and YB-71, and the black paint D-111. The effects of low earth orbit, which include those induced by UV radiation and atomic oxygen, varied significantly with each paint and its location on LDEF. For example, samples of Chemglaze A276 located on the trailing edge of LDEF darkened significantly due to UV-induced degradation of the paint's binder, while leading-edge samples remained white but exhibited severe atomic oxygen erosion of the binder. Although the response of S13GLO to low earth orbit is much more complicated, it also exhibited greater darkening on trailing edge-samples compared to leading-edge samples. In contrast, YB-71 and D-111 remained relatively stable and showed minimal degradation. This report examines the performance of these paints as determined by changes in their optical and physical properties, including solar absorptance as well as surface chemical changes and changes in surface morphology. It also correlates of these optical and physical property changes to the physical phenomena that occurred in these materials during the LDEF mission.				
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PREFACE

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INTRODUCTION

The Long Duration Exposure Facility (LDEF) was initiated in 1976 as an exposure facility for various materials to the low earth orbit (LEO) environment. The 30-ft long, 14-ft diameter spacecraft consisted of 57 experiments and was placed in a 255 nmi orbit by the Space Shuttle Challenger on April 7, 1984¹ for almost six years. It was returned to earth on January 20, 1990.

Spacecraft in LEO, such as LDEF, are exposed to an environment that includes UV radiation, atomic oxygen, electrons, protons, thermal cycling, and micrometeoroids and debris. However, compared to synchronous orbits, the fluxes of electrons and protons are small, and the effects are, therefore, minor in comparison to atomic oxygen and UV irradiation effects.² The spacecraft encounter an apparent flux of atomic oxygen of 10^{15} atoms/cm²-s with a kinetic energy of approximately 5 eV due to the average orbital velocity of 8 km/s through the static low earth atmosphere.³ However, the entire LDEF spacecraft was not exposed to the same atomic oxygen flux. The leading edge (LE) of the spacecraft, which was nearly perpendicular to the velocity vector ($\sim 8^\circ$ off normal), received a much higher flux than the trailing edge.⁴ Consequently, leading-edge samples on LDEF were exposed to an atomic oxygen fluence of as much as 8.74×10^{21} atoms/cm², while trailing-edge (TE) samples were exposed to an atomic oxygen fluence as low as 1.13×10^3 atoms/cm².^{5,6} This difference allows the comparison of the synergistic effects of UV radiation and atomic oxygen exposure on LE samples to UV radiation exposure on the TE samples.

The materials experiment M0003 was designed, built, and integrated by the Aerospace Corporation Mechanics and Materials Technology Center as principal investigator, and was designed for the study of the effects of the space environment on current and developmental spacecraft materials. The M0003 subexperiment 18, one of a collection of 8 subexperiments from the Aerospace Corporation Laboratories, consists of 12 samples located on trays D9 (LE) and D3 (TE). These samples included two white thermal control paints, S13GLO (four samples; two on LE, two on TE) and YB-71 (LE, TE), and the black thermal control paint, D-111 (LE, TE). In addition, we were able to section additional samples from the signal conditioning unit (SCU) covers (painted with S13GLO) and the Experiment Power and Data System (EPDS) sunshields (painted with Chemglaze A276, another white thermal control paint) from trays D8 (LE) and D4 (TE), which provided us with numerous samples for destructive analyses. Initial results from this experiment have been previously reported.⁷

A summary of the solar absorptances for the thermal control paints are listed in Table 1. Chemglaze A276 and S13GLO, which are both white thermal control paints with organic binders, exhibited large increases of their solar absorptance on the trailing edge, while the leading edge either decreased slightly (Chemglaze A276) or showed a moderate increase (S13GLO). In contrast, YB-71 and D-111 contain inorganic binders and exhibited little degradation. This report, therefore, focuses on the effects of low earth orbit on Chemglaze A276 and S13GLO.

Table 1. Summary of Solar Absorptances and UV/Atomic Oxygen Fluences

Sample	Location	Solar Absorptance	UV (Sun-hr)	Atomic Oxygen (atoms/cm ²)
S13GLO	Control	0.147	-----	-----
	D9(LE)	0.232	11,100	8.72×10^{21}
	D9(LE)	0.228	11,100	8.72×10^{21}
	D3(TE)	0.458	11,100	1.32×10^{17}
	D3(TE)	0.473	11,100	1.32×10^{17}
	D8(LE-SCU)	0.257	9,400	6.93×10^{17}
	D4(TE-SCU)	0.496	10,400	9.32×10^4
A276	Reference	0.282	-----	-----
	D8(LE-SS)	0.228	9,400	6.93×10^{17}
	D4(TE-SS)	0.552	10,400	9.32×10^4
ZOT	Control	0.130 (est)	-----	-----
	D9(LE)	0.182	11,100	8.72×10^{21}
	D3(TE)	0.182	11,100	1.32×10^{17}
D111	Control	0.971	-----	-----
	D9(LE)	0.933	11,100	8.72×10^{21}
	D3(TE)	0.968	11,100	1.32×10^{17}

BACKGROUND

CHEMGLAZE A276

Chemglaze A276 is a white thermal control paint manufactured by Lord Corporation that incorporates a titanium dioxide pigment in a polyurethane binder. This paint was used on LDEF as a thermal control coating on the Experiment Power and Data System (EPDS) sunshields; these covers were used to protect data system instrumentation for other experiments. These covers were located on the leading edge (row 8) and trailing edge (row 4) of the spacecraft; row 8 was located 30° from the perpendicular of the atomic oxygen vector, and row 4 was located 30° from the perpendicular of the wake region. Consequently, these trays were exposed to different levels of UV radiation and atomic oxygen; samples from row 8 (referred to as leading-edge samples) were exposed to 9400 equivalent sun hours of UV radiation and an atomic oxygen fluence of 6.93×10^{21} atoms/cm², while samples from row 4 (referred to as trailing-edge samples) were exposed to 10,400 equivalent sun hours of UV radiation and an atomic oxygen fluence of 9.32×10^4 atoms/cm².^{5,6}

Experiments from Shuttle missions STS-5 and STS-8 demonstrated the effects of atomic oxygen exposure on material degradation.⁸⁻¹¹ Whitaker reported the effects of atomic oxygen on several paints from the STS-5 mission, including Chemglaze A276.¹² Based on SEM results, she noted that the Chemglaze A276 developed a porous surface, probably due to the atomic oxygen reacting with the polyurethane binder. However, the total atomic oxygen fluence incident on the samples was only 9.9×10^{19} atoms/cm², which is significantly less than the fluence that the leading edge of LDEF received. Additionally, the limited duration of the STS-5 Space Shuttle flight did not permit the evaluation of long-term UV radiation effects.

Other LDEF investigators have reported the effects of atomic oxygen and UV radiation on Chemglaze A276. Pippin¹³ reported that the polyurethane binder was eroded by atomic oxygen, leaving the white pigment exposed. Wilkes and Hummer¹⁴ also reported that A276 exposed to atomic oxygen remained white, while samples on the leading edge of LDEF that had protective overcoatings and, therefore, only received UV radiation exhibited the same UV darkening effects.

The effects of UV radiation on the optical properties of titanium dioxide have been investigated previously.¹⁵ The reflectance spectra of titanium dioxide degrades significantly more in the visible than the IR region, but almost completely recovers to the pre-irradiation values after exposure to an oxidizing atmosphere. This suggests that any UV-induced damage to the Chemglaze A276 pigment could recover upon return of the LDEF spacecraft to earth or on interaction with atomic oxygen.

S13GLO

S13GLO is a white thermal control paint manufactured by IITRI Corporation that incorporates a zinc oxide pigment in a methyl silicone binder. The ZnO pigment is encapsulated with potassium silicate for increased stability in the space environment. Our samples consist of two leading-edge and two trailing-edge samples (trays D9 and D3) plus samples sectioned from the leading- and

and two trailing-edge samples (trays D9 and D3) plus samples sectioned from the leading- and trailing-edge signal conditioning unit covers (trays D8 and D4). Consequently, we were able to access many samples for destructive laboratory evaluations.

Zinc oxide was originally thought to be one of the white pigments most stable to UV irradiation in vacuum.¹⁶ However, in 1965 serious doubts arose due to discrepancies between ground-based and in-flight experiments.^{17,18} As a result, it was determined that the original zinc oxide-based silicone coatings (S-13) were not as stable as first predicted. This instability has been attributed to the formation of an easily bleachable (by oxygen) infrared absorption band (~700-2800 nm).¹⁹ This damage was not observed by post-exposure reflectance measurements performed in air since exposure to the atmosphere resulted in a rapid and complete recovery of the UV-induced damage.²⁰

Since the UV-induced infrared absorption band develops rapidly in zinc oxide and is easily reversed upon exposure to oxygen, it has been suggested that the infrared phenomenon is not related to bulk phenomena but is associated with the photodesorption of oxygen. Gilligan¹⁹ explained the infrared optical behavior of ZnO on the basis of a free-carrier absorption mechanism. Absorbed photons create electron-hole pairs in a "depletion zone" with the holes discharging adsorbed oxygen from the surface of the pigment particles. The zinc oxide pigments, therefore, become electron rich with the electrons accumulating in the infrared-active conduction band, resulting in an increase in the infrared absorption.

The methyl silicone binder itself does not offer an effective barrier to photodesorption reaction on the surface of zinc oxide since it does not "wet" the pigment particles. Consequently, a method was developed to reactively encapsulate the zinc oxide pigment particles with potassium silicate to provide stability to the surface. Studies have shown that the reactively-encapsulated zinc oxide pigment greatly reduces UV-induced infrared degradation.²¹

There is additional UV-induced degradation observed in the S13GLO paint system due to degradation of the silicone binder. When exposed to UV radiation, the methyl silicone binder exhibits induced ultraviolet-visible absorption. Only a portion of this damage observed in S13GLO recovered upon exposure to oxygen,^{21,22} indicating that the degradation is not limited to bleachable surface defects, but may be the result of bulk polymer degradation.²¹ Gaseous products have been observed to evolve during exposure of a methyl silicone/TiO₂ paint system to UV radiation in vacuum and are primarily hydrocarbon molecules. These hydrocarbon molecules are a result of bulk degradation of the methyl silicone binder.²³

Previous atomic oxygen experiments on Shuttle missions STS-5 and STS-8 did not reveal any noticeable degradation to S13GLO.¹² Solar absorptivity and scanning electron microscope (SEM) photographs did not indicate any atomic oxygen erosion of the surface of S13GLO.

EXPERIMENTAL

Samples of Chemglaze A276 and S13GLO from LDEF were studied to determine the effects of atomic oxygen and UV radiation on these materials. Both leading- and trailing-edge samples were compared to control samples since the atomic oxygen fluence varied significantly with location on LDEF. Optical properties, surface morphologies, and surface chemistry were investigated.

Changes in the optical properties of the materials, especially solar absorptance, are the primary indicators of degradation after exposure to atomic oxygen and UV radiation. Optical measurements of the samples were obtained using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. The diffuse reflectance spectra between 250 and 2500 nm were used to calculate the solar absorptances of each sample. This information allowed us to quantify the change in performance of these thermal control coatings.

Atomic oxygen erosion of these materials was a concern, based on previous studies.¹²⁻¹⁴ The surface morphologies of the samples were compared using a JEOL JSM-840 Scanning Electron Microscope (SEM). It was necessary to coat the samples with carbon prior to analysis since they were non-conducting. The results allowed us to compare the effects of the atomic oxygen impingement on the surface of the leading-edge samples.

Changes in surface composition and structure were investigated using X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Analysis (EDAX), and Fourier-Transform Infrared Analysis (FTIR). A VG ESCALAB MK II multiprobe instrument was used for XPS analysis, which yielded surface elemental compositional information. Additional elemental analysis of the surface was obtained by EDAX using instrumentation located on the SEM. Structural information, in addition to limited chemical compositional information, was given by FTIR; the FTIR analysis was performed by the diffuse reflectance method using a Nicolet MX-1 infrared spectrometer. These three analytical techniques complemented each other and aided in our investigation of the degradation mechanisms of these coatings.

The degradation mechanisms were also investigated by UV exposure of leading-edge and reference samples in a space environmental effects chamber in the Mechanics and Materials Technology Center at Aerospace. UV irradiation was performed in vacuum ($\sim 5 \times 10^{-8}$ torr) using a 1000-W xenon-mercury lamp (spectral output > 230 nm) passing through a water filter and a fused-silica window. The samples were exposed for 10 days at a rate of 2 to 3 times the output of the sun over the UV range of 200 to 400 nm (the xenon-mercury lamp has a spectral output comparable to the sun at wavelengths above 230 nm but is significantly less than the sun below 230 nm). This flux resulted in a total fluence of approximately 480 to 720 equivalent solar hours, depending upon their location on the sample table.

RESULTS

CHEMGLAZE A276

Samples of Chemglaze A276 used in this study were sectioned from the EPDS sunshield covers. The reference samples were sectioned from aluminum panels provided by Rockwell Corporation that were prepared after LDEF was returned to earth. Variations in surface preparation, pigment particle size, and paint thickness²⁴ can lead to inherent differences between the LDEF samples and our reference sample; therefore, any conclusions based on a comparison to the reference material should be made cautiously.

The effects of low earth orbit on Chemglaze A276 can be seen in Figure 1. The difference in appearance of the samples is significant; the trailing-edge sample has darkened considerably, while the leading-edge sample has remained white. These differences are also shown in the reflectance spectra in Figure 2 and the calculated solar absorptances in Table 1. The solar absorptance of the trailing-edge sample increased significantly during the LDEF mission. Since the trailing edge of the spacecraft was exposed to predominately UV radiation with limited atomic oxygen exposure, the observed degradation was assumed to be UV-induced. Similarly, preliminary observations indicated that the synergistic effects of atomic oxygen and UV radiation resulted in the leading edge sample of Chemglaze A276 remaining white.



Figure 1. Chemglaze A276-painted sunshields flown on D4 (TE) on left and D8 (LE) on right.

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Figure 1 Chemglaze A276-painted sunshields thrown on L4 (L1) on left and L5 (L2) on right

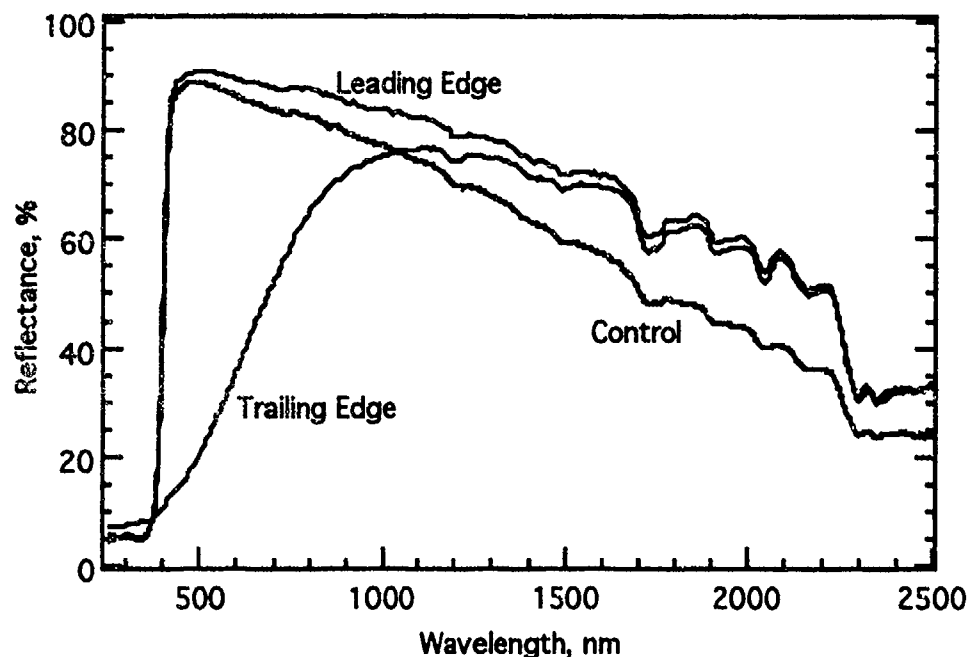


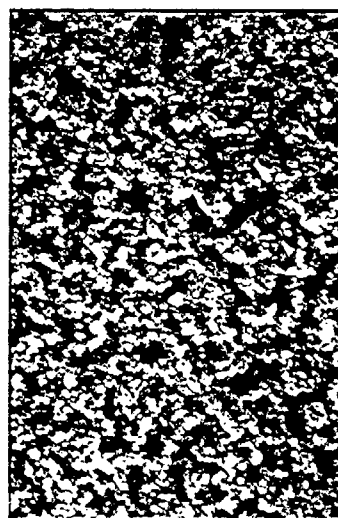
Figure 2. Reflectance spectra of Chemglaze A276 used as a white thermal control paint on the sun shields located on trays D8 (leading edge) and D4 (trailing edge) of LDEF.

Leading Edge

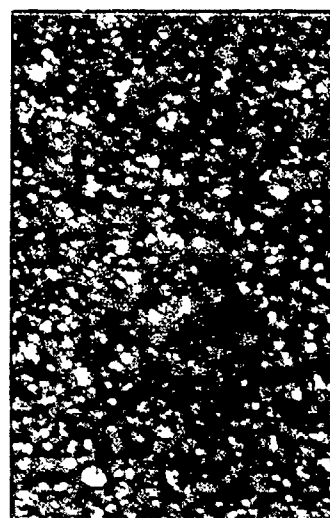
Although it appears from Figure 1 that the optical properties of the leading-edge samples remained unchanged during the mission, optical measurements show that its solar absorptance actually decreased. Inspection of the SEM photographs in Figure 3 show the effects of atomic oxygen on the surface of the leading-edge samples. The polyurethane binder has been eroded away by the atomic oxygen, leaving a surface of titanium dioxide pigment particles. Sample analysis using EDAX confirm that the surface of the leading-edge sample is titanium-rich. EDAX shows a much stronger carbon signal for the trailing-edge sample, which is attributed to the organic polyurethane binder (Figures 4-5).

The increase in the leading-edge solar absorptance can be explained if we consider the refractive indices of the individual components. For the pristine paint, the titanium dioxide pigment particles are embedded in the polyurethane binder. After atomic oxygen exposure, the binder has been eroded from the surface, leaving the pigment particles primarily surrounded by air. Scattering in paints is proportional to

$$\frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}, \quad (1)$$



LEADING EDGE



TRAILING EDGE

Figure 3. SEM photographs of surface of Chemglaze A276 paint exposed on LE (left) and TE (right).

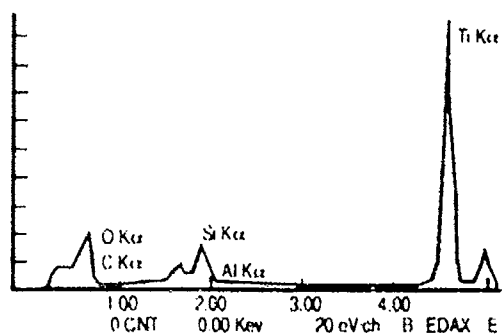


Figure 4. EDAX measurement of Chemglaze A276 leading-edge surface.

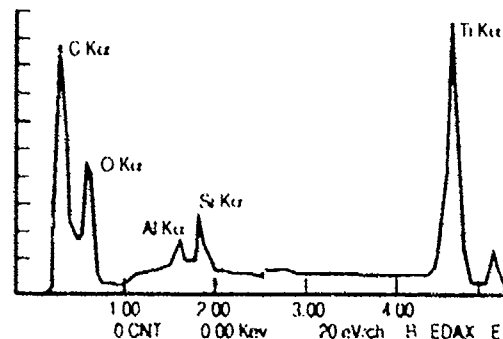


Figure 5. EDAX measurement of Chemglaze A276 trailing-edge surface.

where n_1 is the refractive index of the pigment, and n_2 is the refractive index of the medium around it.²⁴ For titanium dioxide, $n_1 \sim 2.7$, while the refractive index for the polyurethane binder, n_2 , is > 1.0 . Therefore, when the binder is eroded from the surface leaving only pigment particles surrounded by air, where $n_2(\text{air})=1$, the scatter increases. Increased scattering decreases the depth of penetration of the light into the sample, thereby reducing the number of absorption events and reducing the coating's solar absorption. Lowrance and Cox²⁵ discuss the decrease in solar absorptance obtained by eliminating the binder in a pigmented coating and directly sintering the pigment particles together.

Trailing Edge

The major difference between the surfaces of the leading- and trailing-edge samples is the erosion of the polyurethane binder from the leading-edge sample; the surface of the trailing-edge sample still contains binder. An obvious difference is the glossy appearance of the TE sample compared to the chalky LE sample, indicating the changes in paint composition. Combined with the knowledge that the trailing edge of LDEF was exposed to primarily UV radiation, it is most likely that the increase in solar absorptance of the trailing edge is due to UV degradation of the polyurethane binder. Previous investigators have shown that exposure of polyurethanes to ultraviolet radiation results in autoxidization of the urethane chains to a quinone-imide structure. A consequence of these chemical changes is a deepening color from colorless to yellow to amber, and on extensive exposures even to a brown.²⁶ These results are consistent with our observations of the Chemglaze A276 samples from LDEF, as well as those by other LDEF investigators.²⁷⁻²⁹

By exposing leading-edge samples that had surfaces eroded by atomic oxygen (causing binder loss) and, therefore, pigment-rich, such as leading-edge samples, and previously unexposed virgin paint, we were able to show that the degradation does indeed occur in the binder. A rather interesting sample is shown in Figure 6. This sample is from the leading edge of the spacecraft; the opening in the sample is a bolt hole. The area adjacent to this hole was shielded by the bolt head from atomic oxygen impingement, and, therefore, still contains binder on the surface. The rest of

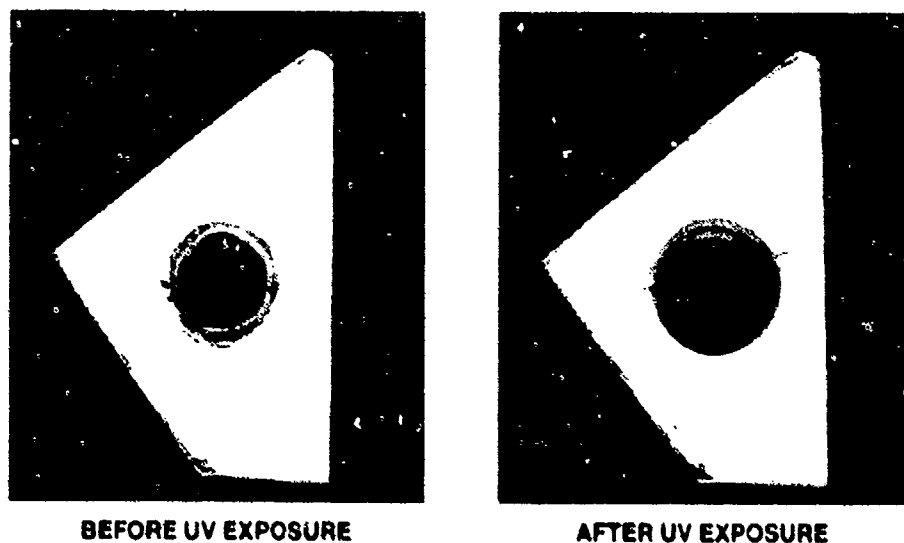


Figure 6. Response of protected Chemglaze A276 to UV radiation.

the sample surface, however, is predominantly titanium dioxide pigment. As the photographs show, the area immediately adjacent to the hole has darkened after the laboratory UV exposure, while the rest of the sample is unaffected. Pre- and post-irradiation solar absorptances of the samples, listed in Table 1, clearly show that the samples affected by the UV radiation are those that contain binder on the surface. The solar absorptance of the leading-edge sample remained fairly constant during UV irradiation, while a virgin paint sample darkened considerably.

S13GLO

Initial observations showed considerable differences between leading and trailing-edge samples, as shown in Figures 7 and 8. Both sets of samples did degrade in the space environment, as evidenced by comparison of the exposed sample regions to the masked regions under the mounting hardware. As with Chemglaze A276, the optical properties of the trailing-edge samples degraded more severely than the leading-edge samples; the trailing edge discolored significantly from white to brown, while the leading-edge samples appeared slightly off-white to tan in color.

The solar absorptances of the two samples, calculated from reflectance spectra obtained in our laboratory (see Figure 9), confirm that the trailing-edge samples darkened much more than the leading-edge samples. The solar absorptance of the trailing edge has increased threefold from an initial value of 0.15 (see Table 1). The leading edge has also degraded, but its solar absorptance has only increased to 0.23. Almost all of the degradation occurs in the visible and ultraviolet wavelengths, with very little degradation occurring above 1200 nm. The absorption peaks above 1200 nm have been identified as methyl silicone (binder) absorption peaks and are present in leading-edge, trailing-edge, and control samples.

Unlike the case with Chemglaze A276, we do not observe any gross difference in the surface morphologies of S13GLO leading and trailing-edge samples. Scanning electron microscopy (SEM) photographs of the leading and trailing-edge surfaces are shown in Figures 10 and 11. At high magnification (5000X) the surface morphologies of the leading and trailing-edge samples appear similar. At lower magnification (100X), however, we see evidence for two different cracking networks on the leading edge, while only one cracking network appears on the trailing edge. Also, the degree of cracking, or cracking density, appears to be much greater on the leading edge. The nature of these cracking networks is not well understood, although elemental mapping with EDAX indicates that the cracks are rich in silicon and depleted in zinc.

Surface analysis of S13GLO using XPS indicates that oxidation of both the leading and trailing-edge sample surfaces has occurred relative to the control sample, as shown in Table 2. The change in O:Si ratio, combined with a Si2p binding energy shift, strongly supports a change from silicone to silica as the predominant surface species on the LDEF samples. It is interesting to note that the O:Si ratio for both the leading and trailing-edge samples has increased to roughly the same values, even though the atomic oxygen fluence on the surfaces varied by 16 orders of magnitude. Surface carbon has been "lost" relative to O and Si, particularly on the leading edge, probably due to the replacement of methyl groups with oxygen in the methyl silicone binder. The amount of carbon lost, however, is related to the atomic oxygen fluence, as indicated by the C:Si ratio of the samples. Erosion of surface layers of silicone binder is also consistent with increased K and Zn signals on both leading and trailing-edge paint.

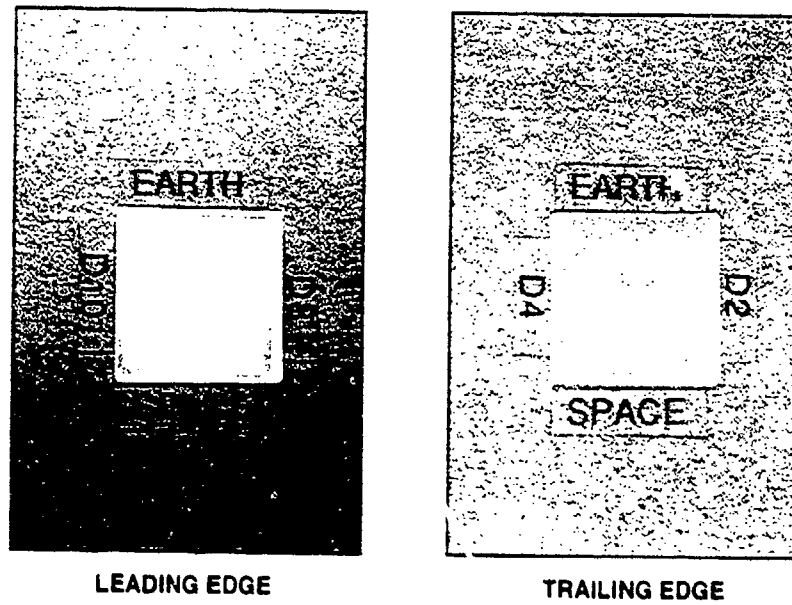


Figure 7. Comparison of S13GLO test samples from trays D9 (LE) on left and D3 (TE) on right.

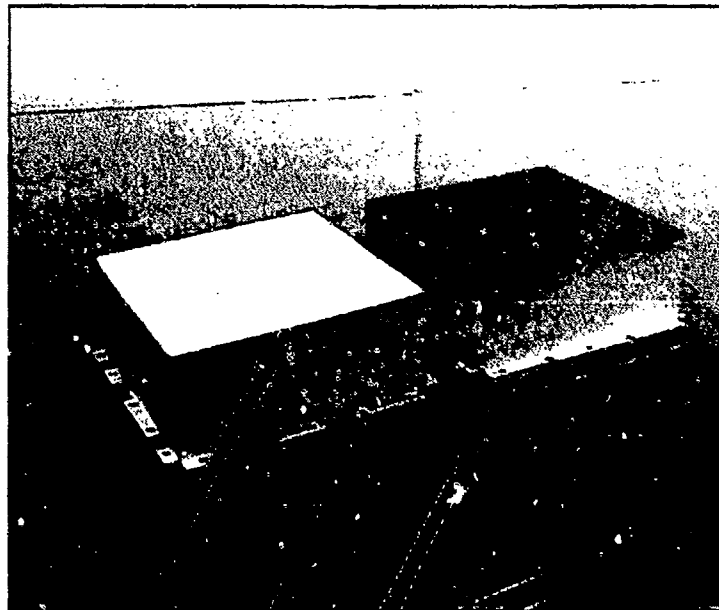


Figure 8. Signal conditioning unit (SCU) covers showing dramatic differences in damage from LE (left) to TE (right).

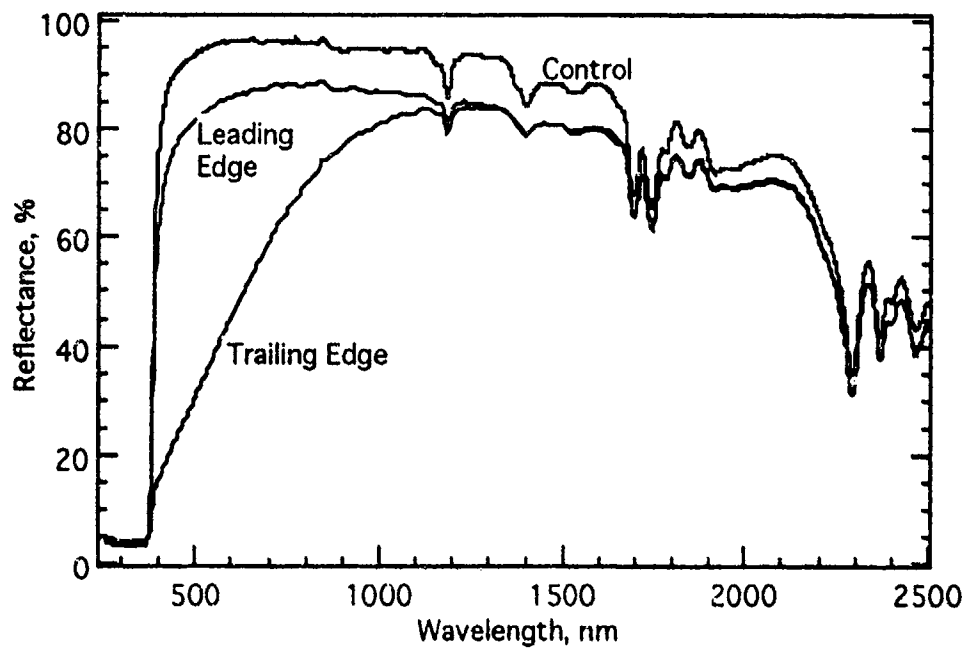


Figure 9. Reflectance spectra of S13GLO test samples from trays D9 (LE) and D3 (TE).

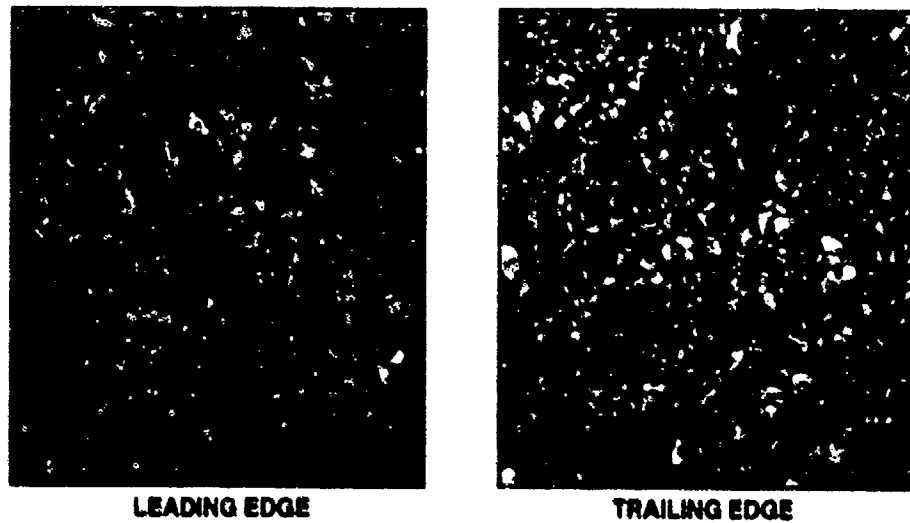


Figure 10. SEM photographs of surfaces of S13GLO on LE (left) and TE (right) at 5000X.

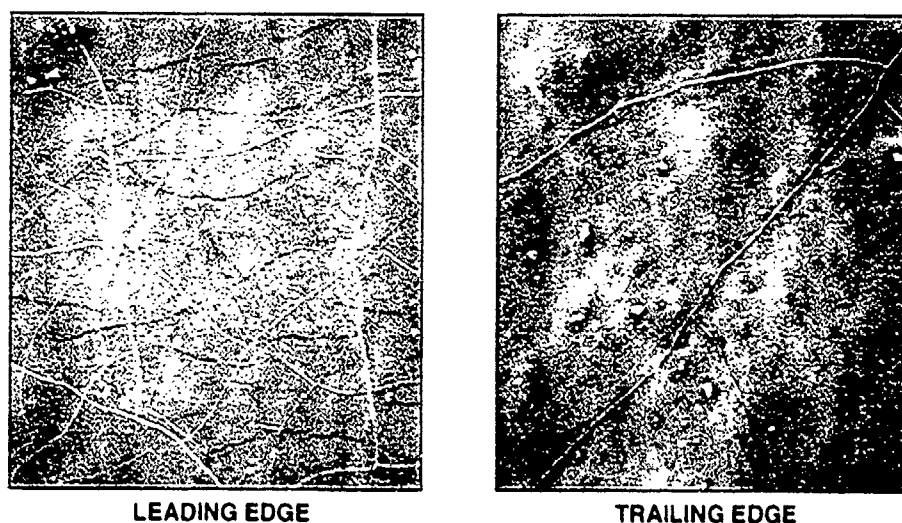


Figure 11. SEM photographs of surfaces of S13GLO on LE (left) and TE (right) at 100X.

Table 2. XPS Analysis of S13GLO Samples

Sample	Surface Mole % (Normalized)										Ratio	
	C	O	Si	K	Zn	N	S	Cl	Na	F	O:Si	C:Si
Control	44	30	26	0.2	nd	nd	nd	nd	nd	nd	1.15	1.69
LE(D9)	12	56	27	1	0.5	2	0.3	0.5	0.3	0.1	2.07	0.44
LE(D9)	13	56	27	1	0.5	2	0.2	0.5	0.3	0.1	2.07	0.62
TE(D3)	28	46	21	0.8	0.3	2	0.4	0.4	0.7	0.5	2.19	1.33
TE(D3)	27	47	21	1	0.2	2	0.4	0.4	0.8	0.4	2.24	1.29
TE(D4-SCU)	33	43	19	0.6	0.3	2.2	0.5	0.4	0.5	0.4	2.26	1.74
TE(D4-SCU)	34	41	21	0.6	0.4	1.9	0.6	0.4	0.3	0.2	1.95	1.62

Significant levels of N, S, Cl, Na, and F were detected as contaminants by XPS on all the LDEF samples, including S13GLO. As Table 2 indicates, the contaminant levels were slightly higher on the trailing-edge samples. However, the contamination most likely did not contribute significantly to the observed degradation of the optical properties of the S13GLO samples. Optical contamination monitors flown on the M0003 experiment indicated small changes in solar absorptance due to contamination consistent with our assertion that the darkening is not related significantly to contamination but is in fact UV-induced degradation.⁷ Additionally, we have been able to cause darkening similar to the observed degradation of S13GLO using UV and vacuum ultraviolet (VUV) irradiation on uncontaminated laboratory samples, as discussed elsewhere in this paper.

Additional evidence for surface oxidation and loss of methyl groups can be seen in the IR spectra in Figure 12. The control sample exhibits absorption peaks characteristic of the methyl silicone

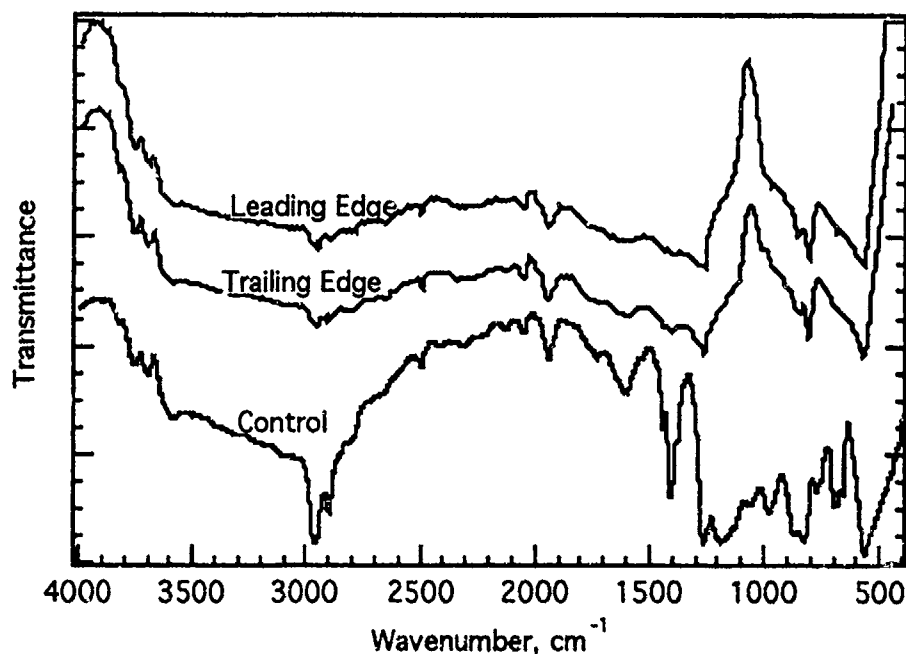


Figure 12. IR spectra of S13GLO samples from D9 (LE) and D3 (TE).

binder.³⁰ However, the IR spectra of both leading and trailing-edge samples differ from the control sample in similar details. In particular, the asymmetric Si-O-Si stretch in methyl silicone, represented by absorption peaks at 1066 and 977 cm^{-1} , has broadened significantly and shifted to ~ 1200 to 1300 cm^{-1} . This broader absorption peak is characteristic of the formation of silica.³¹ Also, the absorption peaks associated with the asymmetric $-\text{CH}_3$ stretch (2965 cm^{-1}), the symmetric $-\text{CH}_3$ stretch (2906 cm^{-1}), and the asymmetric $-\text{CH}_3$ deformation (1410 cm^{-1}) in methyl silicone have decreased significantly in the LDEF samples, indicating a loss of methyl groups.

UV Radiation Effects

Changes in the reflectance spectra of both the leading and trailing-edge samples occurs in the region normally associated with degradation of methyl silicone, while little change is observed in the region of the spectra associated with the degradation of zinc oxide. When exposed to UV radiation, methyl silicone shows UV-visible damage.^{21,22} In contrast, zinc oxide exhibits damage in the infrared wavelengths.^{18,19} Even though silicate coatings on zinc oxide greatly reduce UV-induced degradation, it is possible that some degradation of the zinc oxide pigment did occur during the LDEF mission, and that the bleachable nature of these defects resulted in their recovery before the reflectance measurements were made.²⁰ In-flight reflectance measurements of S13GLO samples on LDEF show that the majority of damage does indeed occur in the UV-visible wavelengths,³² which is characteristic of binder degradation. Therefore, the change in the reflectance spectra of both the leading and trailing-edge samples is typical of UV-induced degradation of the methyl silicone binder while there is little evidence to support degradation of the zinc oxide pigment.

Testing of the individual components in our laboratory indicate that UV-induced damage to the methyl silicone binder is the most likely cause of the degradation to the S13GLO samples. When

exposed to UV radiation, only the methyl silicone sample exhibited degradation, while encapsulated zinc oxide pellets remained stable. Samples of S13GLO prepared in our laboratory exhibited an increase in solar absorptance less than 0.04.

Atomic Oxygen Effects

Since both the leading and trailing-edge samples received similar amounts of UV radiation, it is interesting to note that the trailing-edge samples showed a much greater increase in solar absorptance. The role of atomic oxygen must therefore be considered. The leading-edge surface was subjected to an atomic oxygen fluence several orders of magnitude greater than the trailing-edge surface, which may have resulted in chemical and physical differences between the two surfaces.

Surface analyses of the LDEF samples clearly indicates that significant changes occurred in the methyl silicone binders on both leading and trailing-edge samples. The loss of methyl groups, accompanied by an increase in the O:Si ratio, is consistent with an oxidation of methyl silicone to silica. Although the leading-edge surface was exposed to significant amounts of atomic oxygen, it is interesting to note that samples of S13GLO sectioned from the trailing-edge SCU cover on tray D4 also exhibited surface oxidation, even though the reported atomic oxygen fluence of 9.32×10^4 atoms/cm² is significantly less than the amount necessary for one monolayer of coverage ($\sim 10^{15}$ atoms/cm², based on our calculations). The implications of this observation, however, are not fully understood.

The surface oxidation of the methyl silicone binder resulted in changes to the surface morphology of the LDEF samples. The exposure of S13GLO to atomic oxygen resulted in a chemical change (oxidation) of the methyl silicone binder. At high magnification, the surface appears intact since the binder has not been removed from the surface. However, at lower magnifications, the changes become apparent. The surface has developed a cracking network, the extent of which is related to the degree of oxidation as indicated by the atomic oxygen fluence. The most likely explanation is that the cracks developed due to a density change as a result of the oxidation of the methyl silicone binder to silica.

It is not clear why the leading-edge paint surface shows less degradation than the trailing-edge paint surface, although atomic oxygen exposure almost certainly plays a role. One theory is that spalling of the degraded S13GLO surface occurred on the leading edge due to surface oxidation and cracking, thereby exposing a fresh surface. However, this mechanism has not been reproduced in the laboratory and is still under investigation.

SUMMARY

Our investigation of Chemglaze A276 shows that severe degradation occurs due to UV radiation and atomic oxygen interactions. The polyurethane binder in Chemglaze A276 is easily and severely degraded by UV radiation, resulting in a large increase in the material's solar absorptance. Our simulated UV exposure represented only 5 to 8% of the total exposure that the paints on LDEF actually received, but the degradation of the Chemglaze A276 solar absorptance was obvious. In fact, for this test, we did not include the vacuum ultraviolet (VUV) radiation at the shorter wavelengths, which has been shown to result in a greater rate of degradation for some polymer systems.³³⁻³⁶ Additional simulations are in progress.

The polyurethane binder of Chemglaze A276 is also susceptible to atomic oxygen erosion, which creates a surface that is predominantly titanium dioxide pigment. The degree of atomic oxygen erosion depends on the location of the material in relation to the velocity vector in the low earth orbit. Although the thermal control properties of the surface are not deleteriously affected, the surface has lost its physical integrity and is easily damaged upon contact.

Chemglaze A276 is not recommended as a white thermal control paint for spacecraft that require any significant mission lifetimes due to its susceptibility to UV degradation and atomic oxygen erosion. UV radiation causes a significant increase in the material's solar absorption, while atomic oxygen erosion of the binder results in a fragmented surface and could cause particulate contamination to other areas of the spacecraft. Its low cost and ease of application, however, make it much more desirable for boosters and upper stage rockets that do not require long mission lifetimes.

The increase in solar absorptance of S13GLO is due to UV-induced damage of the methyl silicone binder on both the leading and trailing-edge samples; based on our reflectance data, there is no evidence of damage to the encapsulated zinc oxide pigment. This damage is not bleachable and does not recover upon exposure to air, even after one year. Both the leading and trailing-edge surfaces show oxidation of the methyl silicone binder to silica, which is accompanied by a loss of methyl groups and a formation of a cracking network on the surface. The extent of this cracking network depends largely on the atomic oxygen fluence that the surface received. However, unlike A276, there was no preferential removal of the binder by atomic oxygen from the leading-edge surface.

CURRENT WORK

We are continuing our investigation of atomic oxygen interactions with Chemglaze A276 and S13GLO by participating in EOIM III, scheduled to be flown on the Space Shuttle in late 1992. Trailing-edge samples of A276 and S13GLO that were previously flown on LDEF have been included in the sample complement. Pre- and post-test analyses will allow us to study the atomic oxygen effects on these materials and to determine the role of atomic oxygen in the observed degradation of these materials in low earth orbit.

Laboratory simulations of low earth orbit, consisting of UV radiation and atomic oxygen, are continuing. Our facilities in the Mechanics and Materials Technology Center at The Aerospace Corporation allows us to study the effects of UV radiation on unflown and previously flown materials. Atomic oxygen experiments are scheduled for Los Alamos this year; additional atomic oxygen simulations may be performed in facilities at the Aerospace Corporation.

Our investigations are currently expanding to include the YB-71 and D-111 thermal control paints that were originally flown as part of this sample complement.

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TECHNOLOGY OPERATIONS

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