

Organic Matrix Composite Protective Coatings for Space Applications*

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ABSTRACT

Successful use of composites in low Earth orbit (LEO) depends on their ability to survive long-term exposure to atomic oxygen (AO), ultraviolet radiation, charged particle radiation, thermal cycling, and micrometeoroid and space debris. The AO environment is especially severe for unprotected organic matrix composites surfaces in LEO. Ram facing unprotected graphite/epoxy flown on the 69-month Long Duration Exposure Facility (LDEF) mission lost up to one ply of thickness (5 mils) resulting in decreased mechanical properties. The expected AO fluence of the 30 year Space Station Alpha mission is approximately 20 times that seen on LDEF. This exposure would result in significant material loss of unprotected ram facing organic matrix composites. Several protective coatings for composites were flown on LDEF including anodized aluminum, vacuum deposited coatings, a variety of thermal control coatings, metalized Teflon, and leafing aluminum. Results from the testing and analysis of the coated and uncoated composite specimens flown on LDEF's leading and trailing edges provide the baseline for determining the effectiveness of protectively coated composites in LEO. In addition to LDEF results, results from Shuttle flight experiments and ground based testing will be discussed.

INTRODUCTION

As with all other spacecraft materials, successful use of composites in space depends on their ability to survive the various environments encountered during the spacecraft mission. Both AO and particulate radiation can cause a loss of mechanical properties. Thermal cycling induced microcracking results in dimensional stability and mechanical/thermal property changes. The very low vacuum levels of space cause moisture desorption resulting in dimensional changes and possible contamination of sensitive optics. High velocity impacts from meteoroid or space debris may result in cratering, penetration, or structural damage. Choosing the right coating can control or eliminate these environmental effects. The location on the spacecraft (internal vs external), orientation of the composite surface to the spacecraft's ram direction (orbital velocity vector), and the mission profile determine both the need for and the type of protective coating.

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The effects of the various space environments on unprotected organic matrix composites are summarized in the following paragraphs (references 1-4 contain papers discussing additional details).

- Atomic oxygen: AO induced erosion of bare composites is the most detrimental LEO environmental effect. Leading edge erosion has been well documented on the numerous bare composite specimens flown on LDEF's leading or near leading edges (total ram facing AO fluence was 9.09×10^{21} atoms/cm²). Typical depth of erosion loss of unprotected ram facing graphite epoxy (Gr/Ep) was approximately 0.005 inches or one ply of material. This loss resulted in reduced mechanical properties due to the reduced cross-section. AO did not cause any bulk changes in composites.

- Ultraviolet radiation: Minimal effect on composites. Limited to darkening of the surface resin layer

- Meteoroid and Debris: Composites retrieved from LDEF showed numerous impacts with the diameter and depth dependant upon the size and collision velocity of the impactor. Impact features on these composites generally took the form of broken fibers with missing matrix material. In some cases the diameter of the affected volume increased with depth (ref. 5)

- Particle Radiation: The threshold particle radiation dosage for organic matrix composite property degradation is approximately 10^8 to 10^9 rads, well above the total dosage seen by LDEF.

- Thermal Cycling: Thermistors on bare composite specimens flown on LDEF's indicated a maximum and minimum of approximately +180°F and -50°F over the first 4000 cycles of the 32,422 cycles seen by LDEF (ref. 6).

Figures 1 - 3 show three different Boeing built graphite fiber composite spacecraft structures, each possessing different protective coating requirements. Figure 1 is a photo of the Gr/Ep Hubble Space Telescope truss structure. This internal structure is shielded from any external environment with its temperature determined by the various layers of the spacecraft between it and the external spacecraft surfaces. This 252 lb structure highlights a property that composites provide, dimensional stability. The 16 ft focal length between the primary and secondary mirror supports is designed and manufactured to remain within 0.00005 of an inch during the temperature cycling associated with the LEO environment. Figure 2 shows a Gr/Ep antenna designed for use in a geosynchronous orbit (GEO) environment. The 6 ft diameter reflector has a base coating of vacuum deposited aluminum (VDA) overcoated with white inorganic coatings (YB-71 and Z-93). The VDA enhances the rf reflectivity and also serves as a good primer for the two inorganic coatings which provide passive thermal control. This coating scheme was subjected to twenty +250°F to -320°F thermal cycles and then exposed to high levels of particle radiation exposure. Test results met all program requirements. Although this coating scheme provides an excellent AO barrier, because of the GEO mission profile, AO protection was not a requirement. Figure 3 shows a prototype graphite/cyanate ester satellite bus structure designed for small launch vehicles such as Pegasus. This structure requires an exterior coating that 1) rejects heat generated by experiments mounted on decks within the structure and 2) provides protection for the thin exterior composite facesheet from AO induced erosion.

PROTECTIVE COATINGS

The use of a well designed and stable protective coating on externally mounted organic matrix composites both protects the underlying composite substrate from the exterior environment and alters the bare composite optical properties, resulting in reduced temperature extremes. Table 1 shows various protective coatings along with the range of optical properties possible with each coating.

| Material | Solar Absorptance | Thermal Emittance |
|--|-------------------|-------------------|
| Bare Composite | | |
| T300/934 | 0.90 | 0.73 |
| Adhesively Bonded Aluminum Foil | | |
| Bare aluminum foil | 0.08 - 0.17 | 0.03 |
| Chromic acid anodized - 1145 Al alloy | 0.20 - 0.39 | 0.15 - 0.62 |
| Chromic acid anodized - 6061 Al alloy | 0.48 - 0.57 | 0.18 - 0.69 |
| Sulfuric acid anodized - 5657 Al alloy | 0.15 - 0.20 | 0.78 - 0.84 |
| Vacuum Deposition | | |
| Sputtered Al (420Å - 2520Å) smooth Gr/Ep surface | 0.16 | 0.05 - 0.09 |
| Sputtered Al (420Å - 2520Å) rough Gr/Ep surface | 0.24 | 0.19 - 0.30 |
| Vacuum deposited Al | 0.22 | 0.04 |
| Thermal Control Paints | | |
| Z-93 | 0.14 - 0.17 | 0.92 |
| YB-71 | 0.07 - 0.13 | 0.89 - 0.90 |
| YB-71/Z-93 | 0.10 | 0.85 |
| S13G/LO | 0.15 - 0.19 | 0.88 - 0.91 |
| A-276 | 0.21 | 0.87 |
| Other Coatings | | |
| Silverized Teflon (5 mil thick) | 0.06 | 0.81 |
| Silverized Teflon (2 mil thick) | 0.07 | 0.66 |
| Plasma sprayed aluminum | 0.28 | 0.80 |

Table 1. Composite Protective Coatings

Ground based testing provides the initial screening for these coatings. Actual on-orbit exposure data is needed to verify ground based results and develop the necessary design confidence prior to these coatings being applied to spacecraft surfaces. Coatings flown on LDEF provide this data which has become the baseline for predicting coating performance in a LEO environment. It is interesting to note that LDEF was deployed prior to a thorough understanding of the effects of AO on organic composites. The coatings flown on LDEF composite specimens were selected as thermal control coatings. However, the majority of these coatings provided excellent AO protection. The following lists identify composite coatings that have been flown in space and undergone post-flight testing and analysis.

Protectively coated composites flown on LDEF:

- A-276 white titanium dioxide pigment in polyurethane binder with epoxy polyamide primer.
- BMS 10-60: white titanium dioxide pigment in polyurethane binder
- S13G: white zinc oxide in RTV 602 silicone binder (unknown if this was S13G/LO)
- White zinc oxide coating manufactured by General Dynamics
- Z-306: black carbon in polyurethane binder
- Tin/indium eutectic coating
- Leafing aluminum with epoxy binder with an epoxy polyamide binder
- Sputtered coatings: aluminum, aluminum/nickel, SiO₂/nickel, SiO₂/aluminum/nickel, SiO₂/chromium
- Aluminum thermal control tape

Composite coatings (without composite substrates) flown on LDEF:

- Chromic acid anodized aluminum
- Sulfuric acid anodized aluminum
- Z-93: white zinc oxide in a potassium silicate binder
- YB-71: white zinc orthotitanate (ZOT) in a potassium silicate binder
- YB-71 overcoated Z-93 combination
- Adhesively bonded silverized Teflon

Protectively coated composites flown on Shuttle experiments:

- Sputtered coated composites flown on STS-8, STS-41G, and STS-46 (EOIM-3)

TEST RESULTS

The following sections describe the results of ground based testing and testing of retrieved specimens for each category of protective coatings. Table 2 shows representative changes in optical properties of coatings flown on LDEF. The pre-flight values were taken prior to LDEF's deployment, the control values represent data taken on lab specimens after LDEF's retrieval, and the shielded specimens were either specimens facing LDEF's interior protected from the external environment or backsides of composite substrates on LDEF's exterior.

| Specimen | Optical property | Preflight | Postflight (69 month exposure) | | | |
|--|------------------|-----------|--------------------------------|------------|-----------|----------|
| | | | Control | Shielded | Leading | Trailing |
| Bare composite - graphite/epoxy | α | 0.90 | | 0.90 | 0.93 | 0.87 |
| | ϵ | 0.73 | | 0.81 | 0.93 | 0.82 |
| S13G-LO (ref. exp. S0069) | α | 0.18 | | | 0.37 | |
| | ϵ | 0.90 | | | 0.89 | |
| S13G/composite (McDonnell Douglas ctg) | α | | 0.14 | | 0.19-0.21 | 0.34 |
| | ϵ | | 0.90 | | 0.88 | 0.89 |
| Zinc Oxide (General Dynamics ctg) | | | 0.48 | 0.46-0.59* | 0.37 | 0.68 |
| | | | 0.89 | 0.88 | 0.92 | 0.88 |
| A-276 (ref. exp. S0069) | α | 0.25 | | | 0.24 | |
| | ϵ | 0.90 | | | 0.93 | |
| TiO ₂ (A-276?)/composite (McDonnell Douglas ctg) | α | | | 0.31 | 0.29 | |
| | ϵ | | | 0.90 | 0.94 | |
| TiO ₂ (A-276?)/composite (General Dynamics ctg) | | | 0.22 | 0.38-0.45* | 0.35 | 0.59 |
| | | | 0.87 | 0.87 | 0.89 | 0.86 |
| Leafing Aluminum/ composite | α | | 0.67 | 0.66 | 0.60 | 0.75 |
| | ϵ | | 0.79 | 0.78 | 0.73 | 0.78 |
| Z-93 (ref. exp. S0069) | α | 0.14 | | | 0.15 | |
| | ϵ | 0.91 | | | 0.92 | |
| YB-71 (ref. exp. S0069) | α | 0.13 | | | 0.15 | |
| | ϵ | 0.90 | | | 0.89 | |
| YB-71 over Z-93 (ref. exp. S0069) | α | 0.10 | | | 0.11 | |
| | ϵ | 0.85 | | | 0.87 | |
| CAA Al (tray clamps) | α | 0.32 | 0.36 | 0.34 | 0.33 | 0.35 |
| | ϵ | 0.16 | 0.18 | 0.16 | 0.15 | 0.15 |
| CAA Al (Exp S0010) - thick CAA | α | 0.34 | | | 0.35 | |
| | ϵ | 0.75 | | | 0.75 | |
| Silverized Teflon - 5 mil thick | α | | 0.07 | | 0.07 | 0.08 |
| | ϵ | | 0.81 | | 0.78 | 0.81 |

* solar absorptance range due to varying amounts of contamination

Table 2. Optical Properties of Protective Coatings Flown on LDEF.

Anodized Aluminum Foil

Ground Based Testing

A series of NASA LaRC funded research tasks led to the selection of chromic acid anodized (CAA) aluminum foil as the optimum protective coating for Space Station's composite (now aluminum) truss structure. Reference 7 summarizes the findings of these studies into the development of sputter coatings applied directly to composite substrates and on adhesively bonded anodized aluminum foil. Other coatings evaluated included nickel-based coatings. Co-cured 0.002 inch thick CAA foil adhesively bonded to the 2 inch diameter composite tubes with a 0.003" thick layer of epoxy film adhesive was selected as the preferred coating for the following reasons:

- Environmental durability to the LEO environment including retention of foil to composite bond strength and retention of optical properties following 5000 hours of simulated UV exposure.
- Optical tailorability. As shown in Table 1, optical properties can be tailored to individual mission requirements by altering the anodizing parameters and/or aluminum alloy.
- Diameter of impact hole doesn't change with time limiting the amount of composite substrate subject to AO exposure following a meteoroid or space debris impact.
- Provides moisture/outgassing barrier.
- Anodizing and bonding process specifications developed.
- Excellent handling and abrasion resistance.
- Low cost and ease of manufacture.
- Excellent thermal conductivity minimizing temperature gradients due to shadowing of nearby structures.

Testing of Retrieved Hardware

No composites protectively coated with anodized aluminum foil have been flown on retrieved spacecraft hardware. However, CAA aluminum was used as part of LDEF's passive thermal management. The trays, tray clamps, space end thermal covers, and exposed surfaces of the primary structure were all CAA aluminum. This resulted in over 50% of the exposed surfaces on LDEF consisting of CAA aluminum. In addition, several LDEF experimenters flew CAA, sulfuric acid anodized, and dyed sulfuric acid anodized specimens that were anodized to a variety of thicknesses and optical properties. Results indicate that the CAA was very stable in its optical properties, but that contamination caused small increases in absorptance on surfaces exposed to low AO fluences. Sulfuric acid anodized surfaces appeared stable, although very little surface area was available for evaluation and no specimens were exposed to a high AO fluence environment. Only one type of dyed sulfuric acid anodize (Martin Black Anodize) was flown on LDEF. This specimen had increased infrared absorptance characteristics following its trailing edge exposure on LDEF (ref. 8).

Vacuum Deposition

Testing of Retrieved Hardware

Composite substrates sputter coated with a variety of materials and thicknesses were flown on the leading edge experiment S0010, Exposure of Spacecraft Coatings. The combination of materials sputtered onto the Gr/Ep substrates were: aluminum, aluminum/nickel, SiO₂/nickel, SiO₂/aluminum/nickel, SiO₂/chromium, and aluminum/chromium. Figure 4 shows post-flight photos of two 1-in² Gr/Ep specimens flown on this experiment. The specimen on the left was uncoated while the specimen on the right was sputter coated with 600Å SiO₂ over 1000Å nickel. The outer-edge region of both specimens was protected by an aluminum holding fixture. The textured appearance is

the pattern of the breather cloth left in the resin rich surface during specimen fabrication. The 45-degree band pattern, for the uncoated specimen is most likely due to tow-to-tow material variations resulting in different erosion rates. The coated specimen exhibited no mass loss while the uncoated specimen lost 3-4 mils of material. Post-flight testing and analysis showed that while a total coating thickness of 400 Å retarded AO induced Gr/Ep erosion, total coating thicknesses as thin as 800 to 1000 Å eliminated any mass loss (ref. 9). Additional results also showed that rough surface morphology of composites can result in numerous protective coating defects of these ultra-thin coatings (ref. 10).

Space Shuttle flight STS-8, launched in September 1983, flew three sputtered coatings deposited on Gr/Ep substrates. Table 3 shows the various materials, thicknesses, and pre-flight and post-flight optical properties. Post-flight test results show the three coatings were generally unaffected by the 42 hour ram facing (3.5×10^{20} atoms/cm²) Shuttle exposure (ref. 11).

| Specimens | Pre-flight α/ϵ | Post-flight α/ϵ |
|---|---------------------------------|----------------------------------|
| 1600 Å of 0.999% pure nickel | 0.52/0.45 | 0.52/0.45 |
| 600 Å SiO ₂ over 1600 Å nickel | 0.50/0.27 | 0.49/0.27 |
| 800 Å Al ₂ O ₃ over 1800 Å aluminum | 0.29/0.78 | 0.29/0.78 |

Table 3. Optical Properties of STS-8 Specimens

Thermal Control Paints with Composite Substrates

Testing of Retrieved Hardware

Over 55 organic matrix/graphite composite substrates overcoated with thermal control coatings were flown on LDEF. The specific coatings, A-276, BMS 10-60, S13G, Z306, leafing aluminum, zinc oxide mfg by General Dynamics, and an indium-tin eutectic were exposed to leading edge, trailing edge, and shielded environments on LDEF. Laboratory control specimens were also kept for the duration of LDEF's 69 month mission.

M0003-10 Results

LDEF Experiment M0003-10, Advanced Composites Experiment, included specimens supplied by McDonnell Douglas Space Systems Company (MDSSC) and General Dynamics Space Systems Division (GDSSD) to determine the effectiveness of protective coatings. MDSSC evaluated the TiO₂ (post-flight analysis shows this coating to most likely be A-276), S13G (unable to determine if this was S13G/LO), and leafing aluminum coated graphite/polyimide, Gr/Ep, and graphite/thermoplastic substrates. GDSSD evaluated TiO₂ (post-flight analysis and discussions with retired GDSSD personnel determined this coating was most likely A-276), ZnO (this was a proprietary coating developed by GDSSD somewhat similar to the S13G coatings), and an indium-tin eutectic coating (developed by GDSSD as a moisture barrier to prevent on-orbit composite dimensional changes associated with moisture desorption) protecting graphite-fiberglass fabric/polysulfone and graphite/epoxies. Most of the samples were composite strips 3.5 inches long x 0.5 inches wide with the coating applied to all six sides. Pre- and post-flight mass loss data was taken by The Aerospace Company (M0003 experiment integrator). Additional post-flight characterization occurred at Boeing Defense & Space including optical properties, cross-sectioning, and coating adhesion.

The optical properties for the TiO₂ coated specimens were typical of results found on A-276 coatings mounted throughout LDEF and provide an interesting study into the synergistic effects of the LEO environment. The leading edge AO fluences were high

enough to cause enough erosion of the polyurethane paint binder, removing the UV darkened binder seen on the trailing edge specimens. This AO induced erosion kept the UV damaged paint near original pre-flight absorptance levels. However, this erosion leaves the surface layers of the TiO₂ pigment in the A-276 without any binder. While the optical properties had not changed, the surface layers had lost their physical integrity and are easily damaged upon contact. The trailing edge specimens increased in solar absorptance due to the UV exposure darkening the polyurethane resin (no AO "cleansing" of the A-276). Tape peel testing on a leading edge specimen removed the pigment down to the stable binder. No material was removed during tape peel testing of shielded or control specimens. No erosion of the substrates was observed. Post-flight inspection showed that all the GDSSD woven graphite-fiberglass fabric/polysulfone (W-722/P-1700) specimens (coated, uncoated, lab control, and flight) had significant cracking. It is unknown if the cracking was present following cure or whether it slowly developed over time. The cracking was most likely due to coefficient of thermal expansion (CTE) mismatches between the fiberglass, graphite, and polysulfone matrix. On the coated specimens, these cracks extended up through the TiO₂ coating as shown in Figure 5. Photomicrographs taken at 400x appear to show minor AO induced erosion of the composite through the larger cracks on the leading edge.

Figure 6 shows leading edge and trailing edge MDSSC S13G coated composite specimens. The control and trailing edge optical properties were typical of LDEF data with the trailing edge specimen taking on a strongly discolored yellow appearance. The leading edge specimen took on a lightly discolored brown appearance but it experienced a much smaller increase in absorptance than other leading edge S13G/LO specimens. Unlike the A-276, tape peel tests showed no material removed from any of the specimens. Similar cracking was visible in the GDSSD ZnO coated W-722/P-1700 specimens as occurred in their TiO₂ coated specimens.

Figure 7 shows leading edge, trailing edge, and shielded leafing aluminum coated composite specimens. The leafing aluminum coating consists of aluminum flakes in an epoxy binder applied to a primed composite substrate. No other leafing aluminum specimens were flown on LDEF. Like the A-276 coated composites, the leafing aluminum specimens illustrate the synergistic effects of the LEO environment. The decrease in absorptance and increase in emittance for the leading edge specimen is attributed to removal of the epoxy binder exposing additional aluminum flakes. The increase in absorptance for the trailing edge specimen was caused by UV darkening on the epoxy binder. Tape peel testing removed some of the unsupported aluminum flakes on the leading edge specimen. No material was removed during tape peel testing of the control or trailing edge specimens. No erosion of the underlying composites was noted.

The indium-tin eutectic coating was developed as a composite moisture barrier. Minor visual differences between leading and trailing edge specimens with the exposed surfaces becoming dull and discolored compared to the control specimen. No erosion of the underlying composites was noted.

Pre- and post-flight mass loss data was taken by The Aerospace Company for all composite specimens flown on Experiment M0003-10 and all laboratory control specimens. These measurements were made after the samples had equilibrated in a constant temperature and humidity environment which eliminated moisture variations. The majority of the coated composite data is shown in Table 4. Analysis of this data illustrates the effectiveness of the coatings in protecting the underlying composite substrate from AO induced erosion. LDEF data showed that leading edge bare composites underwent a 2% to 4% mass loss. The coatings reduced this mass loss to negligible amounts similar to shielded or lab control specimens.

| Specimen location | Uncoated - % mass change (# of specimens) | Coated - % mass change (# of specimens) |
|--------------------------|--|--|
| Leading edge - exposed | - 2.15 (1) | + 0.02 (2) |
| Leading edge - shielded | - 0.41 (2) | - 0.07 (2) |
| Trailing edge - exposed | - 0.19 (1) | + 0.73 (1) |
| Trailing edge - shielded | - 0.05 (2) | - 0.56 (1) |
| Lab control | - 0.17 (3) | - 0.05 (3) |

Indium-Tin Eutectic Coating on GY70/X-30 Graphite/Epoxy flown by GDSSC.

| Specimen location | Uncoated - % mass change (# of specimens) | Coated - % mass change (# of specimens) |
|--------------------------------|--|--|
| S13G - Celion 6000/polyimide | - | + 0.14 (1) |
| S13G - T300/5208 | - | - 0.12 (1) |
| S13G - T300/P-1700 | - | - 0.02 (1) |
| Leafing Al - T300/P-1700 | - | - 0.41 (2) |
| TiO ₂ - T300/P-1700 | - | - 0.18 (1) |

Various coatings with various substrates flown by MDSSC. All specimens located on leading edge-exposed. No lab controls or uncoated specimens.

| Specimen location | Uncoated - % mass change (# of specimens) | Coated - % mass change (# of specimens) |
|---------------------------------------|--|--|
| S13G - Trailing edge exposed | - | - 0.04 (2) |
| Leafing Al - Trailing edge exposed | - | - 0.11 (1) |
| - Trailing edge shielded | - | + 0.05 (1) |
| TiO ₂ | - | + 0.01 (1) |

T300 Graphite/Polyether Sulfone with various coatings flown by MDSSC. No lab controls or uncoated specimens.

| Specimen location | Uncoated - % mass change (# of specimens) | ZnO Coated - % mass change (# of specimens) | TiO ₂ Coated - % mass change (# of specimens) |
|--------------------------|---|---|--|
| Leading edge - exposed | - 2.80 (2) | - 0.37 (6) | - 0.33 (6) |
| Leading edge - shielded | - 0.63 (2) | - 0.12 (6) | - 0.13 (6) |
| Trailing edge - exposed | - 0.08 (3) | - 0.04 (3) | - 0.03 (3) |
| Trailing edge - shielded | - 0.09 (3) | - 0.03 (3) | - 0.02 (3) |
| Lab control | - 0.07 (4) | - 0.01 (4) | - 0.03 (4) |

Graphite-Fiberglass Fabric (W-722)/P-1700 with ZnO and TiO₂ coatings flown by GDSSD

Table 1. Mass changes for coated composite substrates flown on M0003-10 (data courtesy of The Aerospace Corporation).

M0003-8 Results

The electronics module cover for the leading edge experiment M0003-8 was an 11.75" x 16.75" Gr/Ep panel with thermal control coatings in three of the four quadrants. The following paragraphs summarize findings presented in reference 12. This panel was coated with two white urethane coatings, A-276 and BMS 10-60, and a black urethane coating, Z306. The fourth quadrant was left bare. One inch diameter mounting washers located at the corners and along each side shielded the underlying composite and coating. Temperature extremes were predicted, using pre- and post-flight optical properties, for each quadrant with the results showing maximum and minimum temperatures of 235°F to -70°F for the uncoated quadrant, 205°F to -70°F for the Z306 coated quadrant, and 60°F to -75°F for both the A-276 and BMS 10-60 quadrants. The bare composite lost an average of over 0.003 inches and the white coated quadrants showed no underlying composite erosion due to shielding by the AO stable TiO₂ pigment. The Z306 coating was severely eroded as both the carbon pigment and the polyurethane matrix were eroded by the AO. Some initial attack of the substrate under the Z306 coating was apparent. Extensive microcracking was observed in the black Z306 and bare quadrants. These cracks extended approximately one inch into the two white coated quadrants. The cracks, which appear to be related to thermal stresses, propagate up through the white coatings.

Figure 8 is a 3D plot of the data collected during a laser profilometry scan of a portion of the module cover. The approximately 1 inch square contains a circular region shielded from AO attack by one of the mounting washers. The A-276 coating covers the rear left half of the panel segment. This shows several interesting features including three distinct height levels, contaminant shielded area, and an impact site.

The five most prominent impact sites in this panel were cross-sectioned to investigate coating and substrate damage (figure 9 shows four of these five impacts). All five impacts happened to occur in the A-276 coated quadrant and were severe enough to have breached the coating, exposing the underlying composite. The deepest crater (upper right-hand corner) was over 0.015" deep (three plies). These impacts have many of the same features along with some distinct dissimilarities. Four of the five displayed an inverted hat shape (three very strongly) with the fifth impact site (lower right-hand corner), which does not have this shape, displays extensive crushing and displacement of material. No indications of A-276 coating undercutting by AO were visible in any of the five sites.

As shown in figure 9, pin-hole or impact damage through coatings will expose the underlying composite to AO attack. Reference 13 discusses an analytical approach used to determine reduction in properties of two-inch diameter Gr/Ep tubes from impact damage and subsequent AO induced erosion. Results show a hole diameter ≤ 0.2 " completely through a 0.06" thick tube causes a maximum reduction in the tube's EI (stiffness x inertia) of only 7%.

Space Shuttle flight STS-46, launched in July, 1992, flew an experiment titled Evaluation of Oxygen Interactions with Materials Experiment-3 (EOIM-3) for 42 hours of ram facing exposure (2.3×10^{20} atoms/cm²). Included in the 82 different materials flown on EOIM-3 were three ceramic coated graphite/thermoplastic (PEEK) composites coated with boron nitride/alumina ($\alpha = 0.39/\epsilon = 0.80$), alumina (0.35/0.82), or a plasma sprayed alumina. No measurable changes in optical properties and no visual or mass loss changes occurred for the coated PEEK substrates (ref. 14). AO erosion of the unprotected PEEK was ≈ 2 microns. Post-flight ESCA did show a differentiation of constituents may have occurred during the application of the boron nitride coating. In addition to these EOIM-3 results, two bare Gr/Ep specimens that were previously flown on LDEF were flown again on EOIM-3. One specimen was from the LDEF's trailing edge and the other had been shielded on LDEF, exposed only to vacuum. EOIM-3 post-flight testing showed the LDEF shielded specimen eroded much faster than the specimen that had been exposed on LDEF's

trailing edge. ESCA analysis revealed that silicone contamination existed on the trailing edge specimen which provided some protection against AO erosion (ref. 15).

Ground Based Testing

Reference 16 discusses the results of The Aerospace Corporation's study into the effects of thermal cycling of YB-71 coated Gr/Ep substrates. A second goal of the study was to evaluate the quality of different coating application processes. Five specimens of Gr/Ep coated with VDA were distributed to five participants interested in testing zinc orthotitanate (ZOT) application procedures and the ability of ZOT coatings to withstand thermal cycling from -275°F to +265°F. The participants were Boeing, Hughes Aircraft Company, TRW, JPL, and IITRI (manufacturer of YB-71). While results showed a variation in coating adhesion between the five sets of specimens, all the ZOT coatings performed adequately up to the maximum number of thermal cycles, 440.

Thermal Control Paints without Composite Substrates

Testing of Retrieved Hardware

The Z-93 and YB-71 coatings flown on LDEF were almost unchanged after the 69 month mission. The YB-71 overcoated Z-93 specimen also was impervious to the LEO environment (ref.17) LDEF results show that either coating is an excellent choice for long term LEO exposure. In fact, Z-93 has been selected as the radiator coating for the International Space Station Alpha.

Ground Based Testing

Thermal control coatings possessing a low solar absorptance and high thermal emittance are needed for the Space Station solar dynamic power module radiator surfaces. Eleven candidate materials including white thermal control coatings (Z-93, YB-71, and S13G/LO), silverized Teflon with oxide protective coatings, sulfuric acid anodized aluminum, and a plasma sprayed aluminum oxide coating, were evaluated. Results of extensive ground based testing showed the Z-93 and YB-71 to be the most durable and best performing coatings for this application since they maintained their optical properties and did not show cracking following AO exposure and thermal cycling (ref. 18).

Silverized Teflon

Testing of Retrieved Hardware

Silverized Teflon consists of a 2 mil or 5 mil thick first surface Teflon layer with a 1500Å layer of silver deposited onto the Teflon and a 100Å layer on inconel on the backside to protect the silver. Adhesively backed silverized Teflon is available from Sheldahl and has proven to be an excellent AO barrier. LDEF Experiment S0069 used pressure sensitive acrylic adhesive to adhere the 2 mil thick silverized Teflon to an aluminum facesheet. Post-flight observations showed a brownish discoloration of the silverized Teflon ranging from light to dark brown. The absorptance varied from 0.10 to 0.49 depending on the amount of discoloration. Post-flight testing and analysis showed that the technique used to apply the material to the aluminum covers excessively stressed the material resulting in cracking of the silver and inconel layers. This exposed the adhesive to UV (Teflon is transparent to UV) causing the discoloration. An improved application technique has been developed. Keeping the silverized Teflon flat during release paper removal and reducing squeegee pressure during application of the material to the substrate seems to have eliminated the damage to the silver and inconel (ref.19).

Post flight testing of LDEF ram facing 5 mil thick Teflon thermal blankets showed a Teflon thickness decrease of approximately 1 mil. Ram facing Ag/Teflon took on a milky

appearance and increased surface roughness resulting in decreased specularly. Minimal changes in solar absorptance or thermal emittance occurred for either leading or trailing edges specimens (ref. 20).

Silverized Teflon was also used on hardware retrieved from the Solar Maximum Measurement (SMM) experiment. This hardware was retrieved by the Space Shuttle STS-41C after 50 months in LEO (this Shuttle mission also deployed LDEF). SMM was launched in February 1980 in a 310 nm orbit. After 10 months attitude control malfunctions required that SMM be placed in a spin stabilized orbit until it was repaired 40 months later. By this time the orbit had decayed to 265 nm. Post-flight investigation of the silverized Teflon on the exterior surfaces of retrieved hardware showed changes similar to those found on similar material flown on LDEF. There was no change in absorptance or emittance but the outer surface of the Teflon had become rougher, described by SSM investigators as "bristle like" (ref.21).

SUMMARY

Adhesively bonded coatings - Ground based testing has shown adhesively bonded anodized aluminum foil co-cured or secondarily bonded to composites to be an excellent protective coating. On-orbit optical properties of chromic acid anodized aluminum have proven to be very stable and these properties can be easily tailored to a specific mission requirement by varying anodizing parameters and/or aluminum foil alloy. Aluminum foil also offers the best meteoroid and debris impact resistance of any of the coatings. If a breach of the coating does occur, the foil will limit the amount of AO reaching the underlying substrate. The limited information concerning sulfuric acid anodizing also shows this to be a stable coating but without the wide range of optical properties available in the chromic acid anodizing process. Anodized foil is best suited for tubular or flat structures as it can be difficult to apply to irregular shaped surfaces. In addition, the chromium anodizing facilities are slowly being phased out due to the health hazards associated with chromium.

Silverized Teflon is a widely used thermal control material possessing very low absorptance/emittance ratios. LDEF results showed that the application technique used for applying adhesively bonded silverized Teflon is critical in ensuring good on-orbit durability. Silverized Teflon has shown good long term on-orbit performances with the suitability of using this material to protectively coat composites dependant upon the charged particle or AO fluences seen during the mission (ref. 20).

Vacuum deposited coatings - LDEF results show that extremely thin sputtered coatings offer excellent atomic oxygen protection. Coatings as thin as 800Å eliminated any AO induced erosion of the composite substrate. Sputtering a layer of SiO₂ over the base metal layer provides the required emittance. For these coatings to be effective all composite surface irregularities must be adequately coated. The limitation to these coatings is the complexity associated with the need for vacuum during the coating process.

Thermal control coatings - Most space qualified thermal control coatings will provide the needed environmental protection and optical property retention for short term missions. The organic based coatings, such as S13G/LO and A-276, offer a good coefficient of thermal expansion (CTE) match with composite substrates and good coating/composite adhesion strength. For longer term missions two IITRI coatings, YB-71 and Z-93, provide the necessary protection and retention of optical properties. While no Z-93 or YB-71 coated composites have been retrieved from space for post-flight testing, LDEF data has shown excellent optical property retention and good bond strength retention to aluminum substrates. Successful application of these brittle ceramic coatings to an organic composite

substrate is rather complex, requiring careful application on a contaminate free surface. The application process used on the antennas shown in figure 2 consisted of a layer of VDA applied to the composite surface followed by a layer of hand rubbed Z-93 and then a spray application of YB-71. Boeing is currently developing a ZOT application specification eliminating the need for VDA and hand-rub application of the Z-93. Future flight experiments will be needed to verify this approach.

ACKNOWLEDGEMENTS

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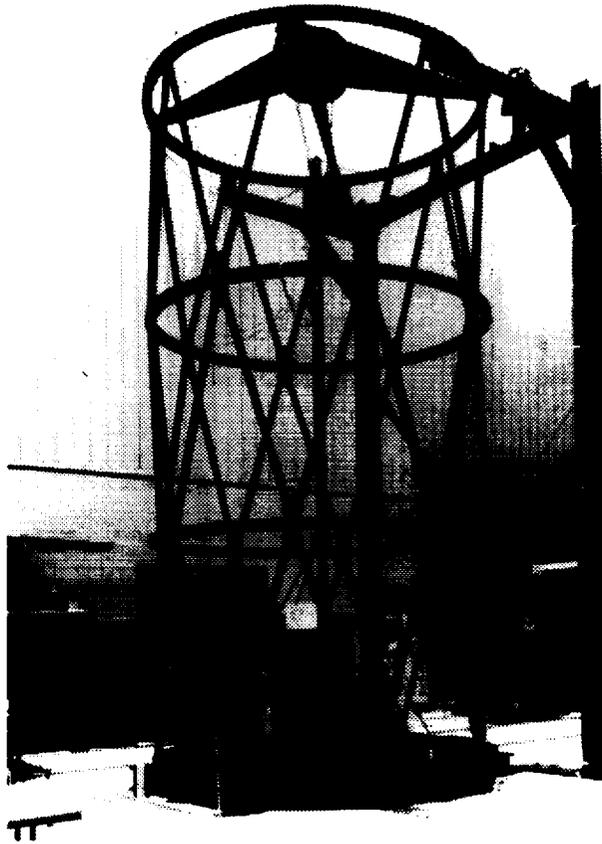


Figure 1. Hubble Space Telescope Optical Truss Assembly

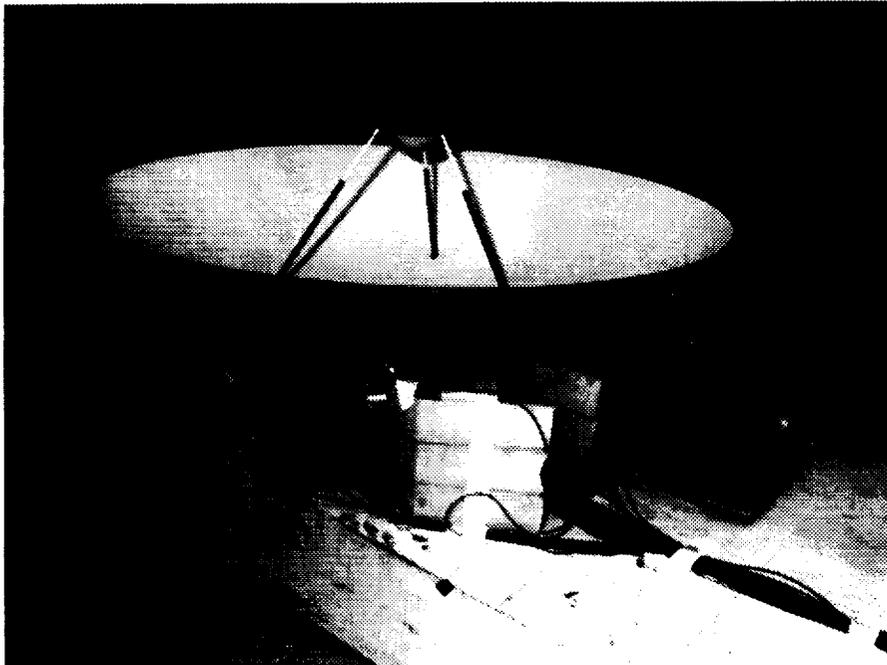


Figure 2. 6 Ft. Diameter Graphite/Epoxy Antenna

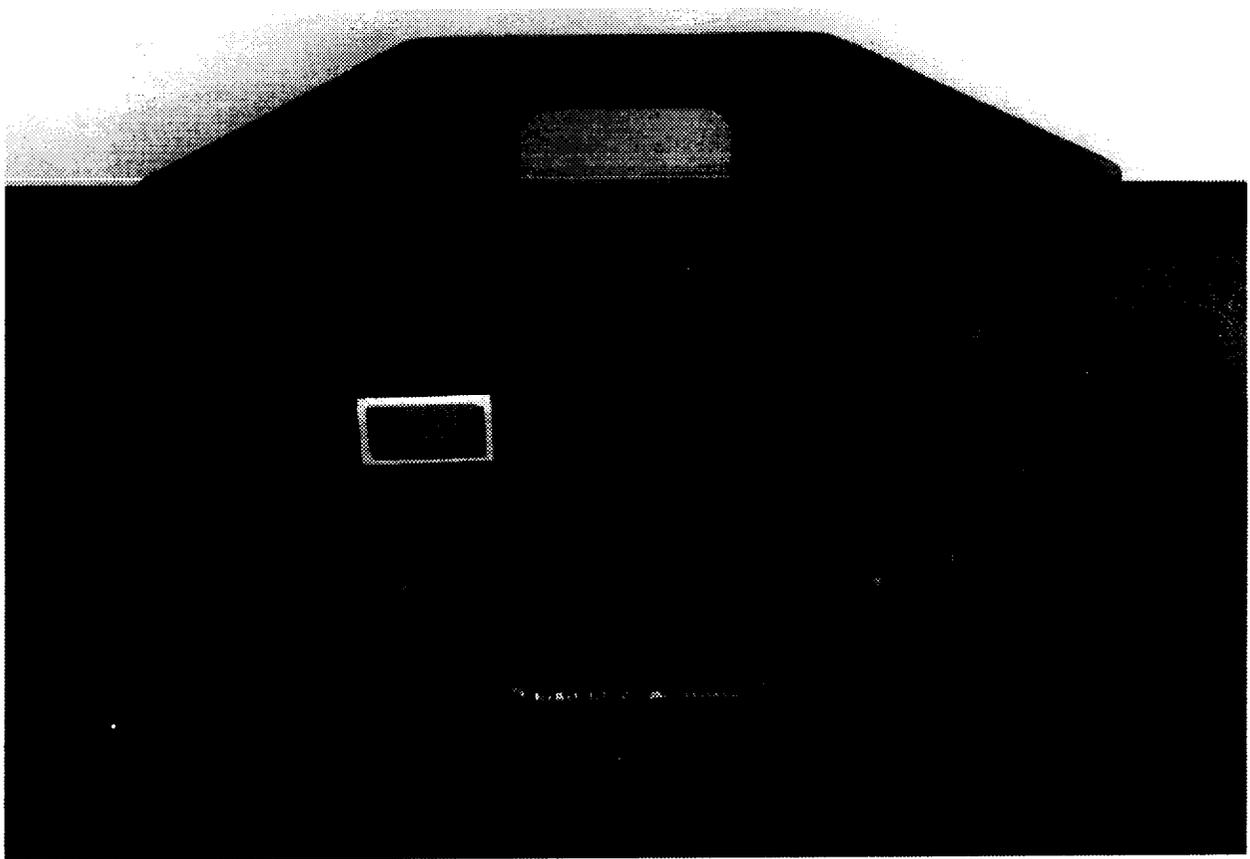


Figure 3. Prototype Composite Spacecraft Bus Structure

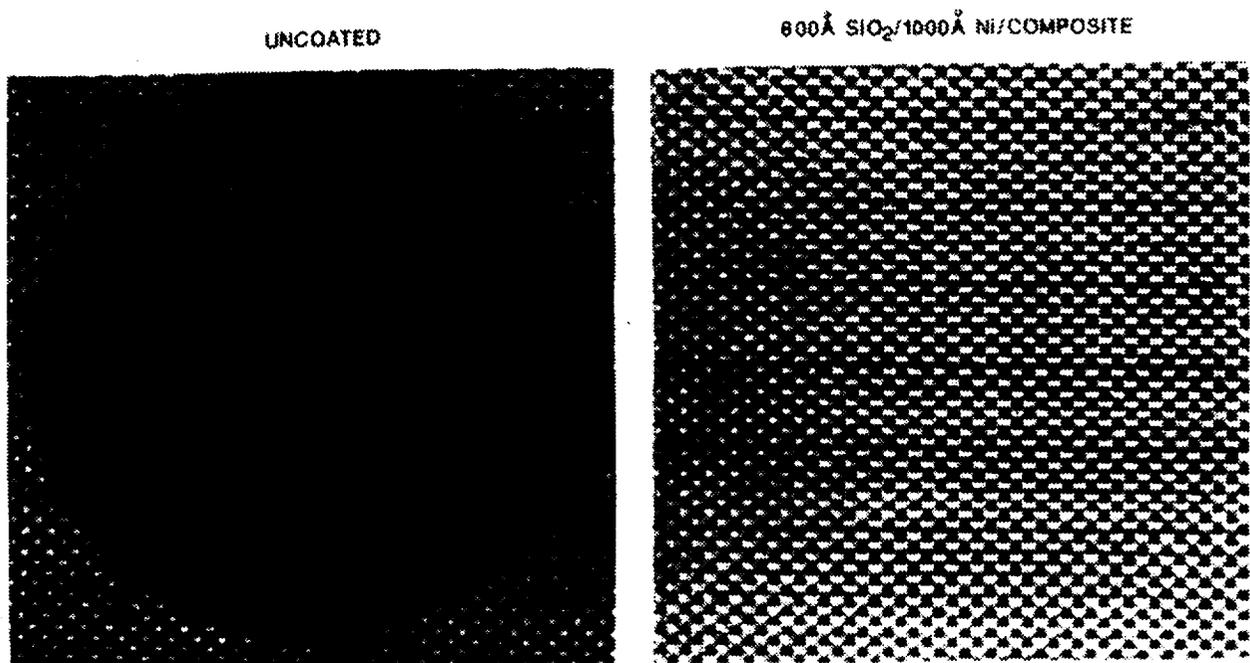


Figure 4. Bare And Protected Graphite/Epoxy Specimens Flown On LDEF's Leading Edge (Photo Courtesy of NASA LaRC)

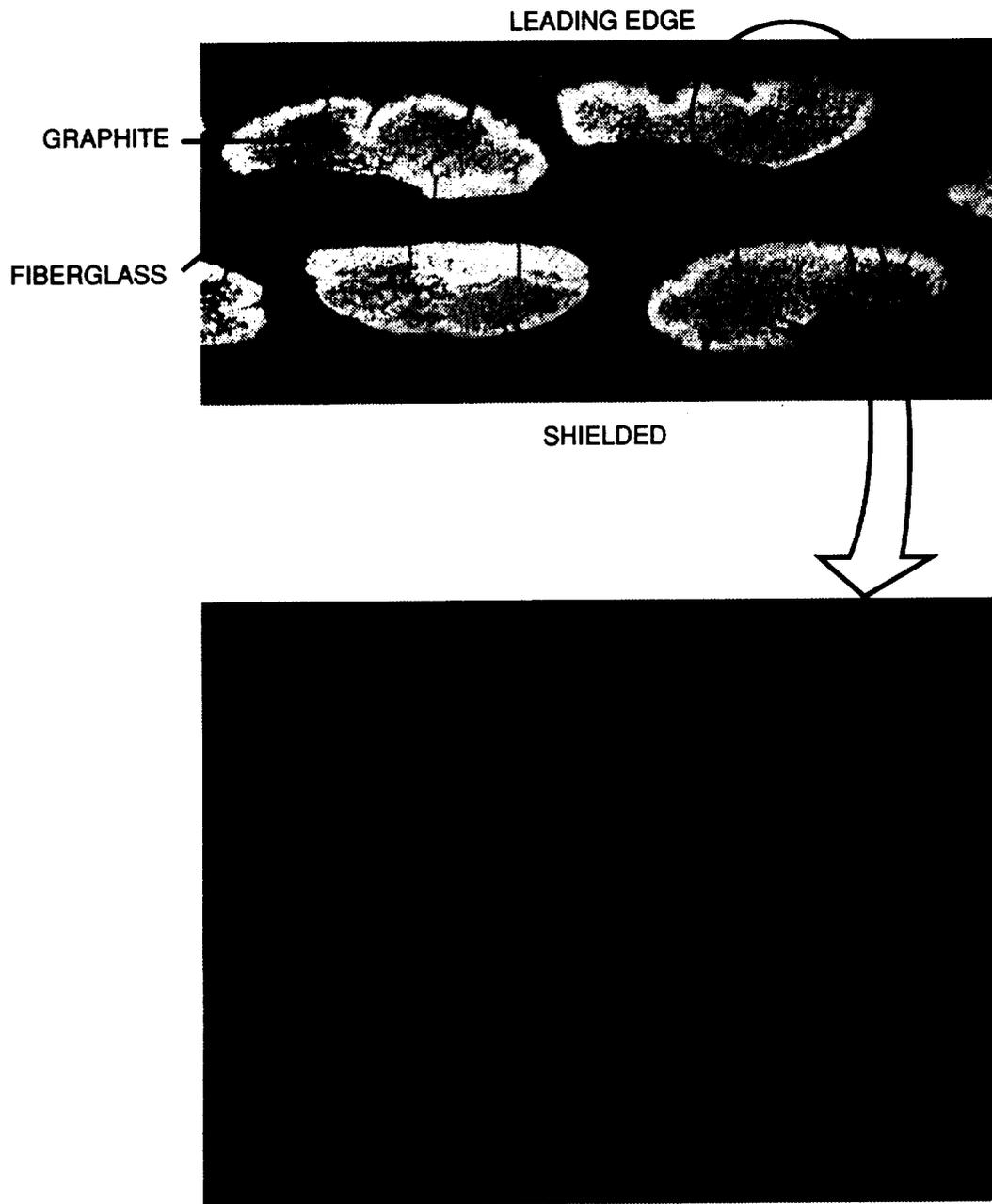
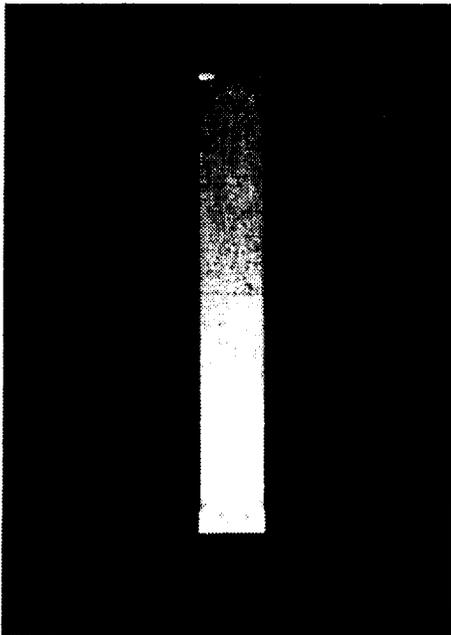


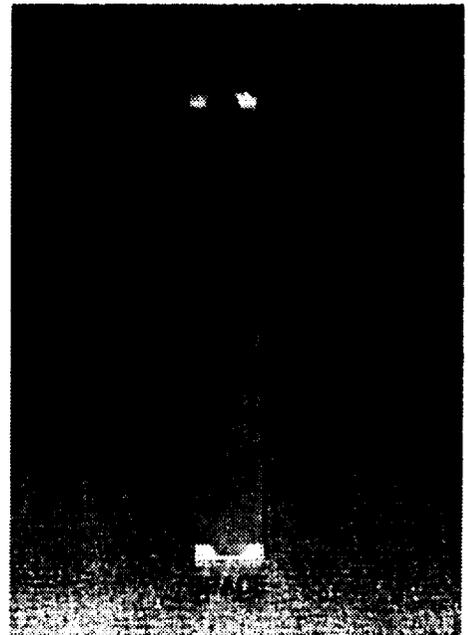
Figure 5. A-276 Coated Graphite-Fiberglass/Polysulfone Composite

OPTICAL PROPERTIES (a/e)

LEADING EDGE
(0.19/0.00)



CONTROL
(0.14/0.90)

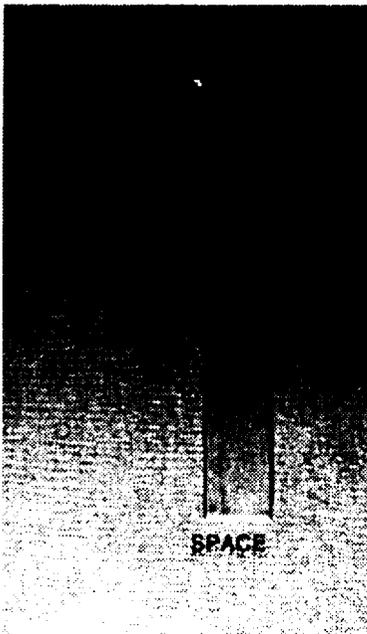


TRAILING EDGE
(0.34/0.89)

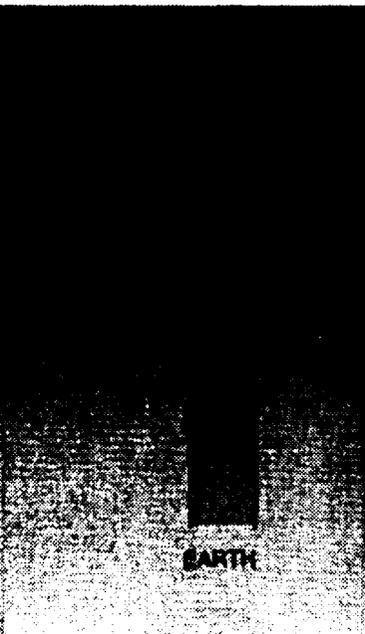
Figure 6. Effects Of LDEF Exposure On S-13G (Photos Courtesy of The Aerospace Corporation)

OPTICAL PROPERTIES (a/e)

LEADING EDGE
(0.60/0.73)



FACING INTERIOR
(0.66/0.78)



TRAILING EDGE
(0.75/0.78)

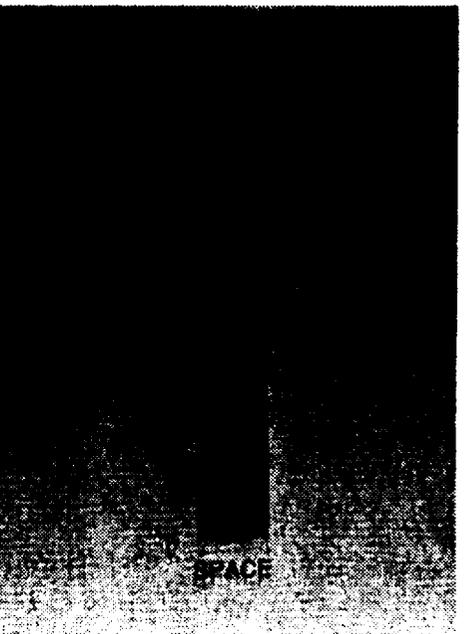


Figure 7. Effects Of LDEF Exposure On Leafing Aluminum (Photo Courtesy of The Aerospace Corporation)

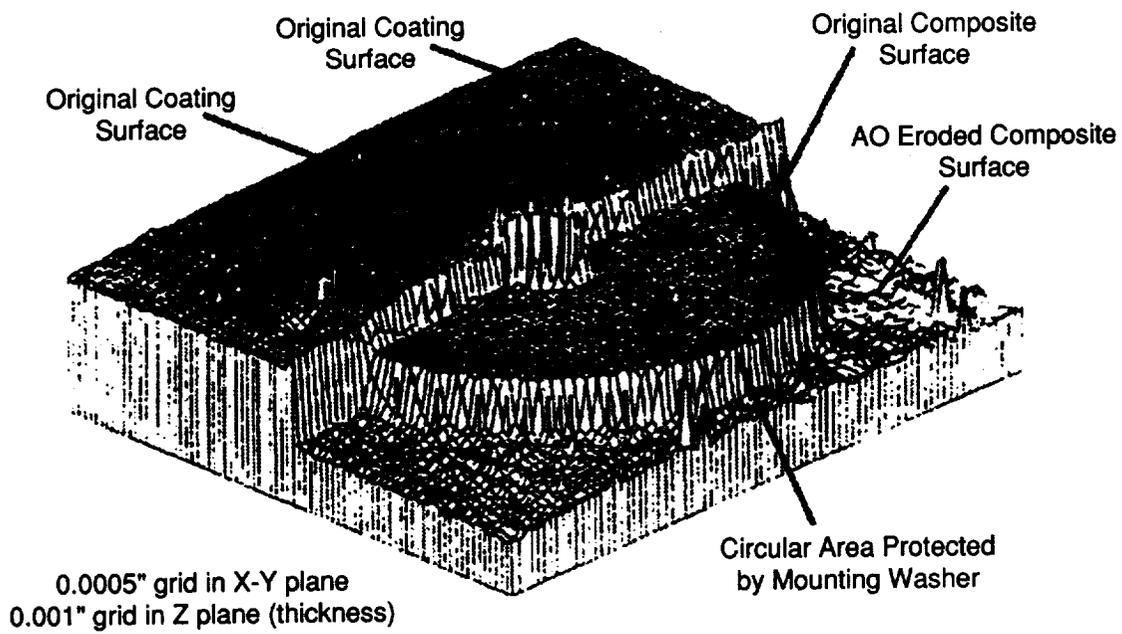


Figure 8. Three-dimensional Plot of Profilometry Measurements Taken From A Partially Coated Graphite/Epoxy Panel

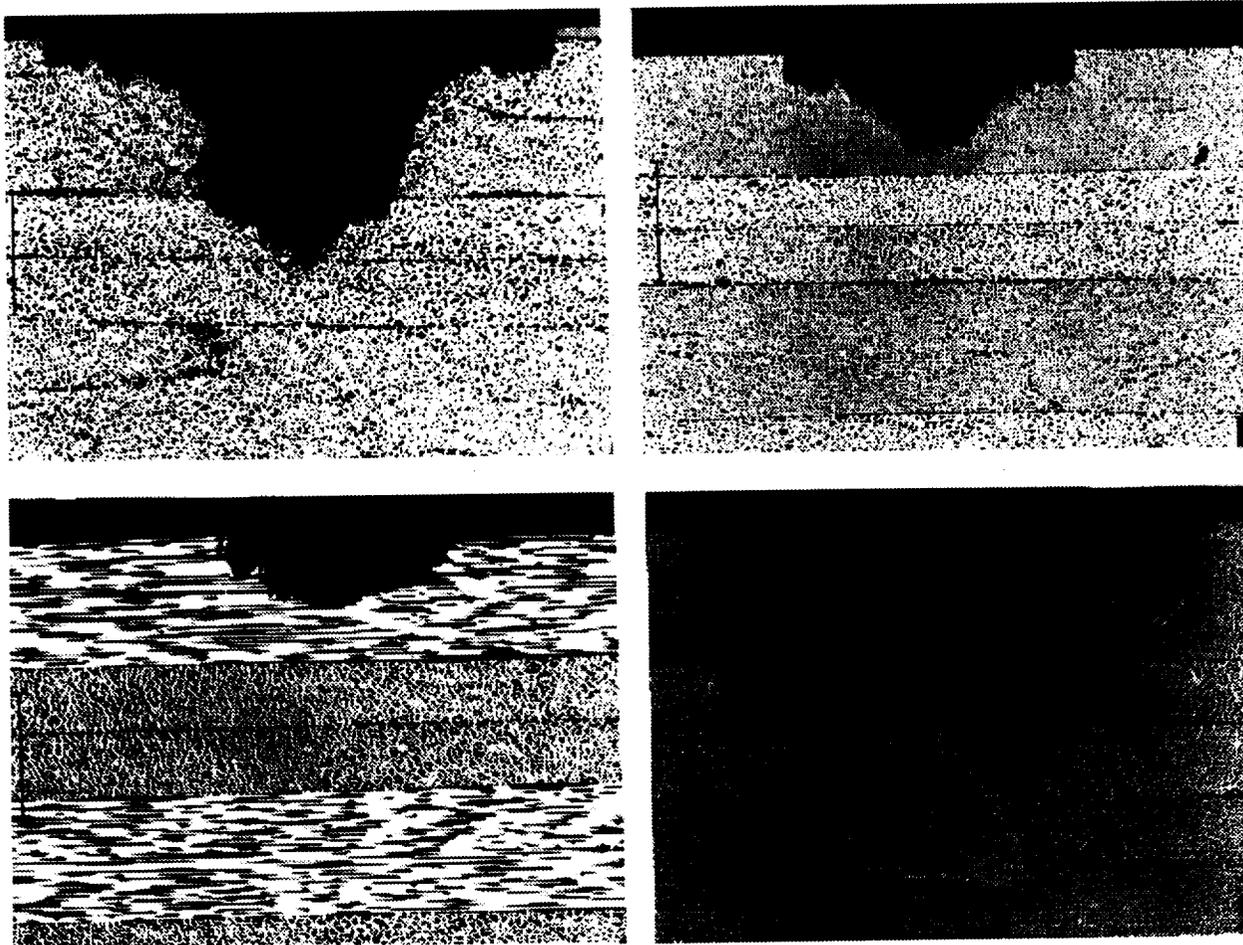


Figure 9. Impact Craters In Graphite/Epoxy