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SELECTED RESULTS FOR LDEF THERMAL CONTROL COATINGS

Johnny L. Golden
Boeing Defense & Space Group
PO Box 3999 M/S 82-32
Seattle, WA 98214-2499
Phone: (206) 773-2055, FAX: (206) 773-4946

SUMMARY

Several different thermal control coatings have been analyzed as part of LDEF Materials Special Investigation Group activity and as part of the Space Environment Effects on Spacecraft Materials Experiment M0003. This paper presents a brief discussion of the results obtained for these materials.

INTRODUCTION

Several thermal control coatings have been analyzed through activities supporting the Long Duration Exposure Facility (LDEF) Materials Special Investigation Group (MSIG), and as investigators on LDEF subexperiment M0003-8. The materials to be discussed here are polyurethane paints (specifically the Chemglaze A276, A971, and Z306 coatings), black chromium plate, chromate conversion coating on aluminum, and chromic acid anodize on aluminum.

The Z306 black and A276 white polyurethane coatings were applied to a graphite epoxy composite panel on experiment M0003-8. This experiment was located on tray D9, with the coatings subsequently exposed to 8.7 x 10^{21} oxygen atoms / cm^2 and to 11,200 equivalent sun hours (ESH) of ultraviolet (UV) radiation (ref. 1). Further description of the graphite epoxy panel and its changes due to environmental exposure are reported elsewhere in this conference publication (ref.2).

The A971 yellow polyurethane coating specimen was a trunnion scuff plate, located between trays C3 and D3 on the LDEF center ring frame. The A971 coating was exposed to 1.3 x 10^{17} O atoms/cm^2 and to 11,100 ESH of UV radiation (ref. 1).

The black chromium plate was from a solar absorber panel, which acted as the heat source for the Cascade Variable Conductance Heat Pipe Experiment A0076. This specimen, located on tray F9, was exposed to 8.7 x 10^{21} AO atoms / cm^2 and to 11,200 ESH of UV radiation (ref. 1).

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The chromate conversion coating on aluminum involved specimens taken from a 6061-T6 aluminum panel used on experiment M0003 as a mounting plate for composite test specimens. The panel was located on tray D3 and was generally exposed to 1.3 x 10^{17} AO atoms/cm^2 and 11,100 ESH of UV radiation (ref. 1). Areas of the panel were, however, partially protected from exposure to these environmental conditions due to the specimens located above its surface. The aluminum panel was not intended as an experimental surface, and so did not have baseline optical properties measured prior to integration into LDEF.

The chromic acid anodized aluminum data was from measurements made on 156 of the LDEF tray clamps, taken from all possible exposure locations on the LDEF structure. The substrate material was 6061-T6, and the clamps were treated by NASA LaRC using a variable anodic process to achieve specific values of solar absorptance and thermal emittance (ref. 3). An initial report on the analysis of the chromic acid anodized tray clamps is available (ref. 4).

RESULTS AND DISCUSSION

Z306 Black Polyurethane

The Z306 polyurethane paint was almost completely eroded away from the composite substrate to which it was applied. The red coloration characteristic of the primer pigment was visible and significant erosion into the composite substrate was observed (ref. 2). Attempts to obtain SEM images of the surface were unsuccessful due to excessive charging, despite having applied three coatings of conductive metal. Based on the specified coating thickness used for the Z306 coating (there were no 'protected' areas of the Z306 on the composite panel to use for an initial surface reference) and the near complete removal of the coating, the erosion rate is estimated to be at least 5 x 10^{-25} cm^3/O atom.

The optical properties of the Z306 coated specimen were measured. The solar absorptance was measured to be 0.93, which is only a 0.02 unit reduction from the initial absorptance of 0.95 for the coating. This was somewhat of a surprising result considering the amount of red primer pigment readily visible on the surface. The thermal emittance was measured as 0.94, which is an increase of 0.04 apparently due to the roughening and diffuse character of the eroded surface.

A971 Yellow Polyurethane

Optical properties have been analyzed for the A971 yellow coating. Solar absorptance was measured to be 0.58, which is about 0.10 higher than what is expected from vendor literature. It is interesting that the absorptance of this particular A971 coating is comparable to that measured for A276 white polyurethane paint exposed to the same environmental conditions. The thermal emittance was measured as 0.87, essentially no change from what is expected for a gloss polyurethane paint without atomic oxygen exposure and consistent with observations for comparably exposed A276 white polyurethane paint.

Black Chromium Plate

Initial analyses for the black chromium plated absorber panel on Experiment A0076 have been reported (ref.5). The panel was observed on-orbit to have a section of the surface covered by a flap of aluminum foil, the flap being a result of atomic oxygen degradation of the experiment's thermal blanket. During deintegration, it was observed that the foil flap had been lost, and that the area which had been covered at the time of retrieval was a tan color. The original color of the panel was a very diffuse black, as can still be observed on protected areas of the panel. The panel surface which was exposed to the space environment for the full mission was observed to be a very dark blue (slate blue), see figure 1.

The optical properties of the various areas on the absorber panel were measured as depicted in figure 2. Emittance was not affected by any of the environmental exposures to the panel. The solar absorptance was reduced slightly on the exposed blue area and was significantly reduced in the tan area.

Contamination was observed to be significant around the periphery of the exposed portion of the panel, with silicon a major component. But there was not an apparent correlation between contamination and the tan discoloration area. SEM imaging of the surfaces also did not seem to provide a clear cause for the different optical properties observed. Based on preliminary Auger emission profiles, it appeared that the tan area on the panel had oxidized relative to both the unexposed black and exposed blue surfaces. It was hypothesized that the discoloration was induced by a thermal effect, caused by the close proximity of the bare aluminum foil flap. The premise for this hypothesis was that the foil flap, with high α/ε ratio and very low thermal mass, became significantly hotter than the absorber panel and accelerated the atomic oxygen driven oxidation of the chromium plated surface (ref. 5).

To test the heating effect hypothesis, one and two dimensional thermal modelling analyses were performed with the plate and foil flap system. The results indicated that

the foil flap, though experiencing 300°F thermal cycles, could not have heated the absorber panel under it to a temperature higher than that achieved by the exposed surface.

With the heating effect hypothesis discredited, surface analysis was again tried in order to illuminate the differences between the blue and tan areas on the absorber panel. Figure 3 is an ESCA surface survey of the iridescent or 'rainbow' area in one corner of the exposed area. Most notable in this survey are the high levels of oxygen, silicon, and carbon, indicative of silicone contamination. Figure 4 is an ESCA survey of the exposed blue area, where the silicon levels are significant but much less than that observed the corners of the exposed area. Figure 5 is a survey of the tan area, which appears to have lower silicon levels than the exposed blue area.

Elemental Auger profiles for the blue and tan areas are shown in figures 6 and 7. The blue area in figure 6 indicates initially chromium and oxygen, changing to mostly chromium metal with sputtering just as the nickel underplate begins to become apparent. The data from figure 6 is consistent with what is expected for both this system and for the unexposed original black surface. The tan area profile in figure 7 was unexpected. Note the scale on the y-axis is 10% of that in figure 6. It appears that the tan area is much thicker and more completely oxidized than the blue area. A consistent picture for this particular coating and the changes it exhibits has not been achieved; the analysis is continuing.

Chromate Conversion Coating on Aluminum

The chromate conversion coating was only partially exposed to the LDEF environment of tray D3. The surface still had the characteristic iridescence observed for chromate conversion coatings. Optical properties of the surface were measured even though there were no initial readings of the surface taken prior to LDEF integration. The solar absorptance of the surface varied between 0.55 and 0.57, which is about 0.1 higher than what has been typical for chromated conversion coatings measured at Boeing. In lieu of what has been observed on other surfaces on the trailing edge of LDEF, it is likely that this darkening of the coating is due to contaminant deposition. The emittance of the surface was measured at between 0.09 and 0.11, which is certainly in the expected range from Boeing experience.

The chromate conversion coating was also analyzed by X-ray absorption spectroscopy (XAS), to determine the amount and oxidation state of the chromium in the coating. XAS indicated that of the chromium in the coating, only 4% was as hexavalent chromium. This appears to be a significant depletion of Cr (VI) when compared to the 24% level typically observed by XAS in fresh chromate conversion coatings.

Hexavalent chromium depletion in conversion coatings is generally associated with a reduction in the corrosion resistance afforded to the aluminum substrate. Therefore,

three 3" x 5" samples of the M0003 chromate conversion coated panel were subjected to the salt spray corrosion test (ASTM B117) for seven days, as is customary for evaluating fresh conversion coatings on aluminum from aerospace processing. The M0003 chromate conversion coating passed the corrosion resistance test, with no pitting observed on any of the three samples. The salt spray result was, therefore, contrary to what was expected from the XAS results. It is possible that the UV-fixed contaminant layer provided some degree of protection to the test specimens during the salt spray test. But because the specimens did "wet" completely in the salt spray test, it is more likely that the conversion coating itself provided a continuous protective barrier, reducing the need for the corrosion inhibition provided by the hexavalent chromium ion.

Chromic Acid Anodize

The results obtained for LDEF tray clamps treated with chromic acid anodize are shown in table 1. The standard deviations for the populations indicate that the results from one environmental condition to another essentially overlap, with slight indication of absorptance increase for the surfaces not subject to significant levels of atomic oxygen. However, even with this slight increase in absorptance, the results indicate that the optical properties of chromic acid anodize are quite stable in the low earth orbit environment.

A276 White Polyurethane

The A276 paint on composite (Experiment M0003, Tray D9) had areas protected from atomic oxygen erosion, where washers were used in the attachment of the panel to support structure. The atomic oxygen eroded the polyurethane portion of the paint in exposed areas, leaving behind a loose agglomeration of paint pigment particles. We were curious to know how deep the atomic oxygen was able to penetrate into this network of pigment particles, or how deep the exposed paint was damaged from a physical integrity perspective.

Specimens from the composite panel were taken from around the protected attachment areas, and the loose pigment on those specimens was removed by rag wiping. The specimens were then measured using laser profilometry. Height profiles from two different areas along the protected-to-unprotected interface are shown in figures 8 and 9. The figure 8 profile was taken perpendicular to the LDEF axis along the surface toward row 10. The LDEF yaw offset gave the incident atomic oxygen direct access to the paint at the washer interface, yielding a steep erosion profile. Figure 9 was also taken perpendicular to the LDEF axis, but along the surface toward row 8 (180° from figure 8). Here the yaw offset allowed the washer to shield the paint from atomic oxygen erosion at the interface, yielding a tapered erosion profile. The total erosion depth measured using these two profiles, plus four additional measurements, indicated atomic oxygen attack

into the A276 paint surface to a depth of about 10μm (0.0004 inch). Correlation has not been established between the depth of attack and the pigment layer porous structure (0.2μm TiO_2 particles, 1-2μm talc particles, 40.6 volume percent solids). It is not certain that this measured erosion depth is the limit for which atomic oxygen can penetrate into the A276 pigment layer. However, it seems likely that this must be the penetration limit based on the tortuous path atomic oxygen would have to follow in order to continue reacting with the paint resin layer.

The UV degradation of A276 paint on LDEF has been discussed previously (ref. 6). A276 on surfaces not exposed to atomic oxygen has exhibited a sharp increase in solar absorptance with UV exposure. Attempts made to locate ground-based test data for comparison with the LDEF results were essentially unsuccessful. Literature data for numerous white coatings (including A276) have been found, but these reports are typically limited to less than 1000 ESH total UV exposure, due to the moderate UV source intensities that must be used. Another limitation is that ground-based test results are from in-situ reflectance measurements, because of the recognized recovery effect that occurs when short-term UV exposure test specimens come in contact with air. The precise extent of reflectance recovery that may have occurred with the LDEF A276 paint specimens is unknown. The present levels of discoloration in the A276 coating have been determined to be due to degradation of the polyurethane resin portion of the coating, a degradation which cannot "recover".

For engineering purposes, it is essential to establish accelerated test criteria which can be used to predict performance life in a cost effective and timely manner. It was for this reason that comparison of the LDEF A276 results to ground-based UV exposure results was attempted. Failing this, a more controversial approach was made in applying the concept of radiation equivalence. Recent measurements have been made at Boeing Combined Radiation Effects Test Center (CRETC) on the A276 paint, concerning the effects of proton/electron radiation on solar absorptance.[1] A276 was irradiated with 40 keV protons and electrons, simultaneously and in roughly equal fluences to prevent sample charging. Significant degradation in solar absorptance was observed in-situ as a function of radiation fluence. For the purposes of trend comparison, the radiation fluence which produced a solar absorptance reading of 0.52 was arbitrarily equated with a LDEF UV exposure of 8300 ESH. All other particulate radiation fluence levels were scaled from this point. The scaled data set was then compared to the results for A276 white paint data from the LDEF tray clamps, as is shown in figure 10. The trends in the data are significantly similar. The comparison of these two sets of measurements is made here partly as a curiosity. But this comparison is made principally to stimulate thought on the concept of radiation equivalence for materials testing, recognizing the significant impact such an approach could have on long-term performance life prediction.

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[1]L. Fogdall and M. Wilkinson, Boeing Defense & Space Group, personal communication of results to be published.

REFERENCES

1. R. J. Bourassa: Atomic Oxygen And Ultraviolet Radiation Mission Total Exposures For LDEF Experiments. Second LDEF Post-Retrieval Symposium, NASA CP-3194, 1993.

2. P. George: Results From Analysis of Boeing Composite Specimens Flown on LDEF Experiment M003. Second LDEF Post-Retrieval Symposium, NASA CP-3194, 1993.

3. R. J. Duckett and C. S. Gilliland: Variable Anodic Thermal Control Coating on Aluminum, AIAA-83-1492. AIAA 18th Thermophysics Conference. June, 1983.

4. W. L. Plagemann: Space Environmental Effects On The Integrity Of Chromic Acid Anodized Coatings. First LDEF Post-Retrieval Symposium, NASA CP-3134, 1992.

5. J. L. Golden: Changes In Oxidation State Of Chromium During LDEF Exposure. LDEF Materials Workshop '91, NASA CP-3162, 1992.

6. J. L. Golden: Results Of Examination Of The A276 White And Z306 Black Thermal Control Paint Disks Flown On LDEF. First LDEF Post-Retrieval Symposium, NASA CP-3134, 1992.

Measurements On Flight Tray Clamps					Data From AIAA-83-1492	Measurements On Unused Clamps
Unexposed	Exposed-Leading	Exposed-Trailing	Exposed-Space	Exposed-Earth		
$\alpha = 0.34$ 0.01	$\alpha = 0.33$ 0.01	$\alpha = 0.35$ 0.02	$\alpha = 0.35$ 0.02	$\alpha = 0.35$ 0.01	$\alpha = 0.32$	$\alpha = 0.36$
$\varepsilon = 0.16$ 0.01	$\varepsilon = 0.15$ 0.01	$\varepsilon = 0.15$ 0.01	$\varepsilon = 0.16$ 0.02	$\varepsilon = 0.17$ 0.01	$\varepsilon = 0.16$	$\varepsilon = 0.18$
$\alpha/\varepsilon = 2.1$	$\alpha/\varepsilon = 2.2$	$\alpha/\varepsilon = 2.3$	$\alpha/\varepsilon = 2.2$	$\alpha/\varepsilon = 2.1$	$\alpha/\varepsilon = 2.0$	$\alpha/\varepsilon = 2.0$

Note: Second Value Is Standard Deviation

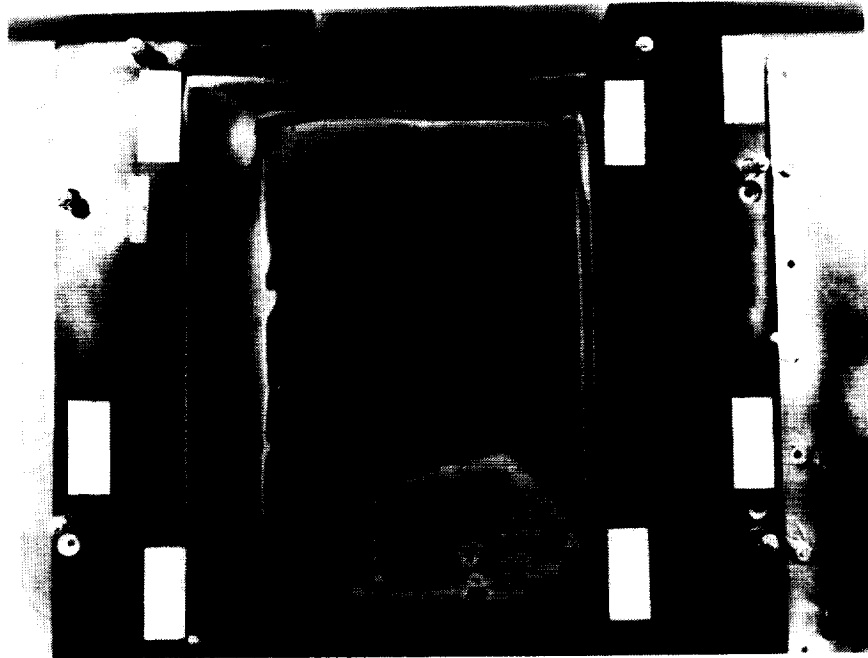Table 1. Averages of optical property measurements for groups of anodized tray clamps.

Figure 1. Photograph of black chromium plated solar absorber panel, experiment A0076, tray F9. (Color photograph is shown on page 1248.)
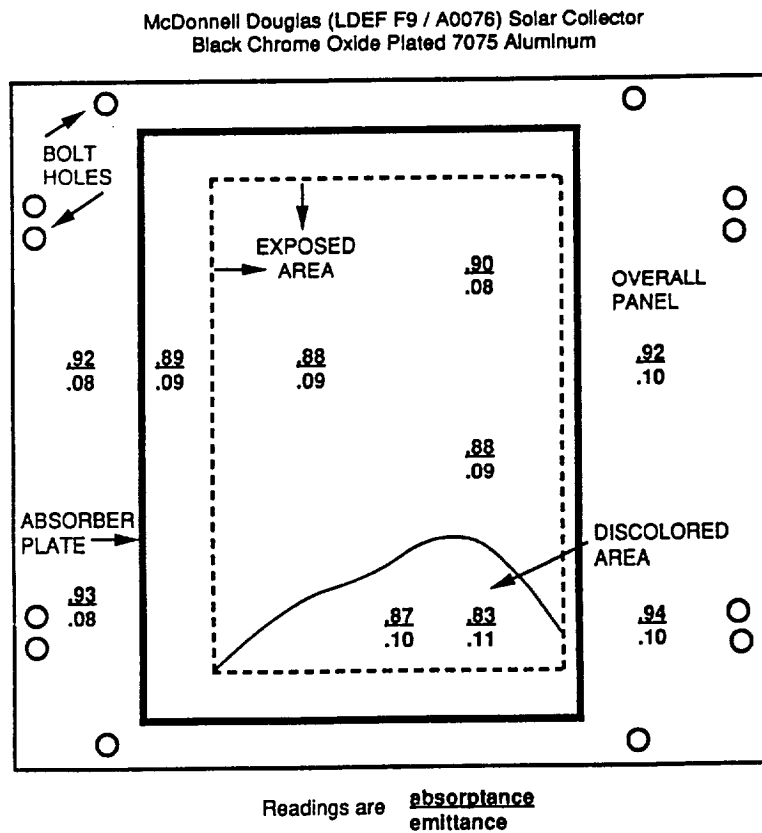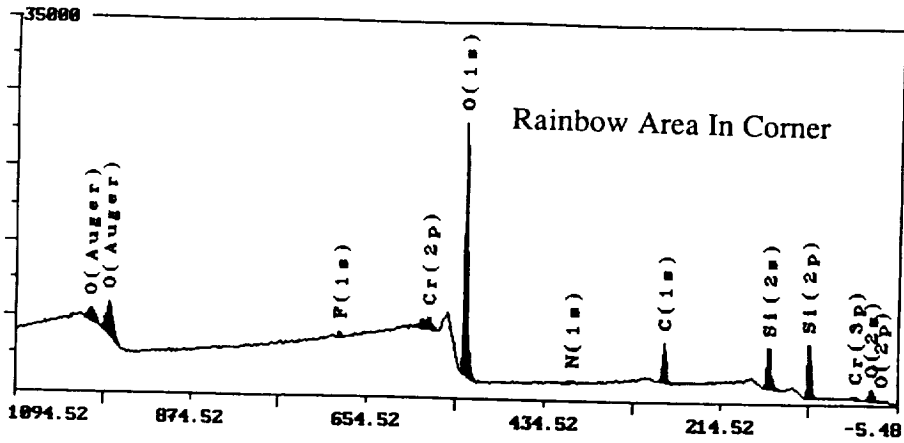

McDonnell Douglas (LDEF F9 / A0076) Solar Collector
Black Chrome Oxide Plated 7075 Aluminum

Readings are   absorptance
                emittance

Figure 2. Optical properties of the black chromium plated solar absorber panel.

Surface Composition Table Summary

Element	Binding Energy	atom %
F (1s)	688.78	0.72 %
Cr (2p)	578.06	1.75 %
O (1s)	532.87	51.70 %
N (1s)	401.12	1.32 %
C (1s)	285.00	20.59 %
Si (2s)	153.69	23.93 %
Total Percent		100.00 %

Figure 3. ESCA survey of a rainbow colored area on the black chromium plated solar absorber panel
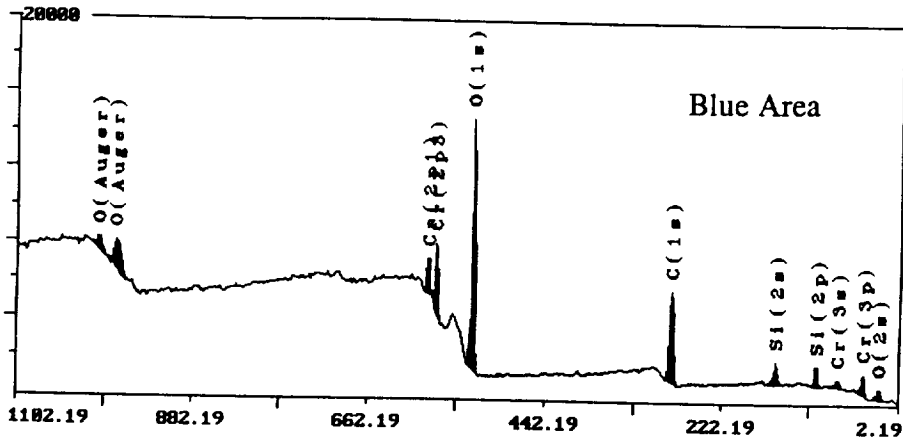
Surface Composition Table Summary

Element	Binding Energy	atom %
Cr (2p3)	578.50	4.16 %
O (1s)	532.68	44.02 %
C (1s)	285.00	43.05 %
Si (2s)	154.37	8.78 %
Total Percent		100.00 %

Figure 4. ESCA survey of a blue colored area on the black chromium plated solar absorber panel
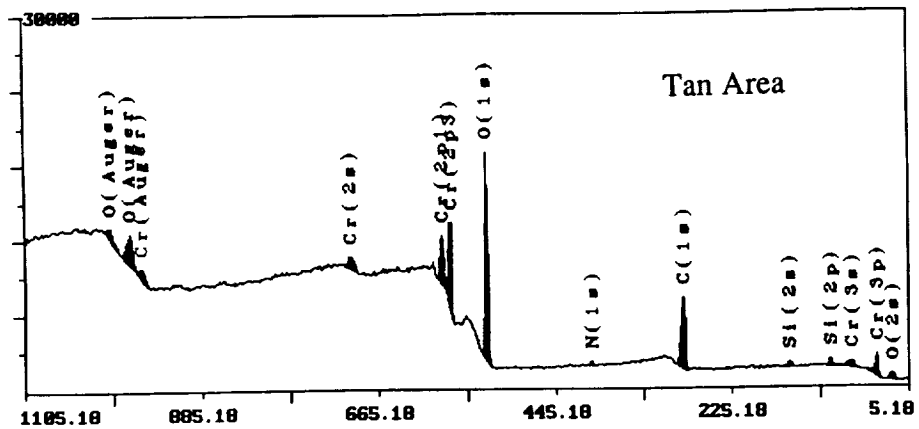
Surface Composition Table Summary

Element	Binding Energy	atom %
Cr (2p3)	577.16	6.29 %
O (1s)	531.82	43.19 %
N (1s)	400.04	0.80 %
C (1s)	285.00	45.14 %
Si (2p)	101.58	4.58 %
	Total Percent	100.00 %

Figure 5. ESCA survey of a tan colored area on the black chromium plated solar absorber panel
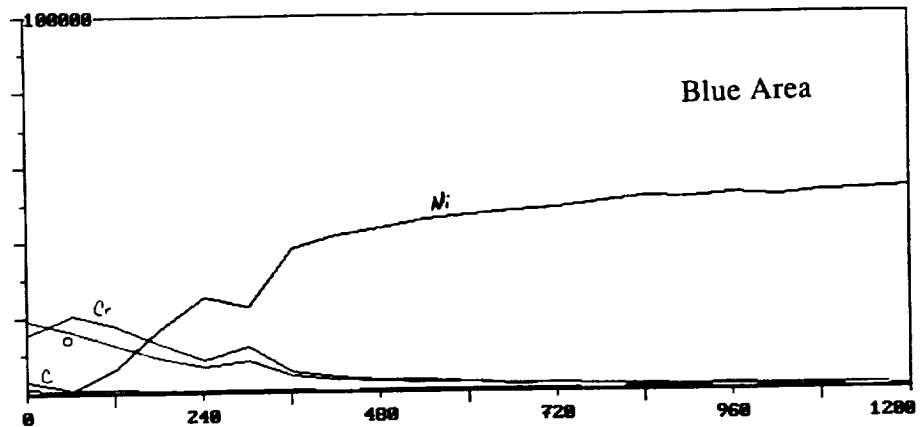

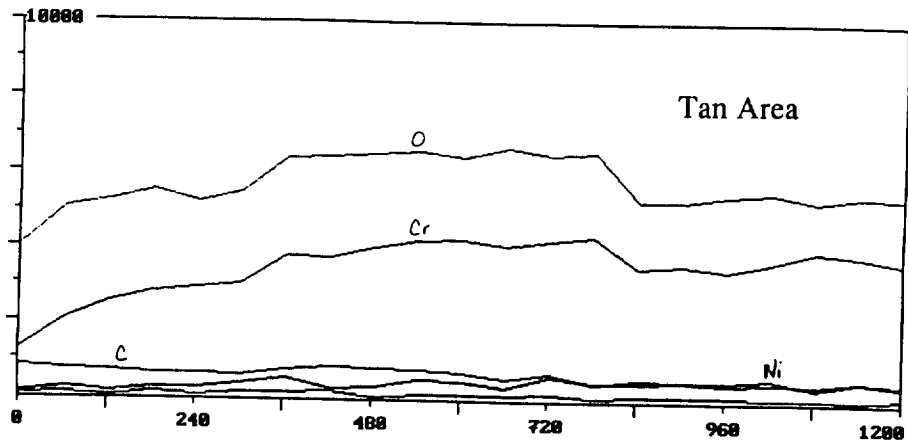Figure 6. Auger profile of blue area on the black chromium plated solar absorber panel.

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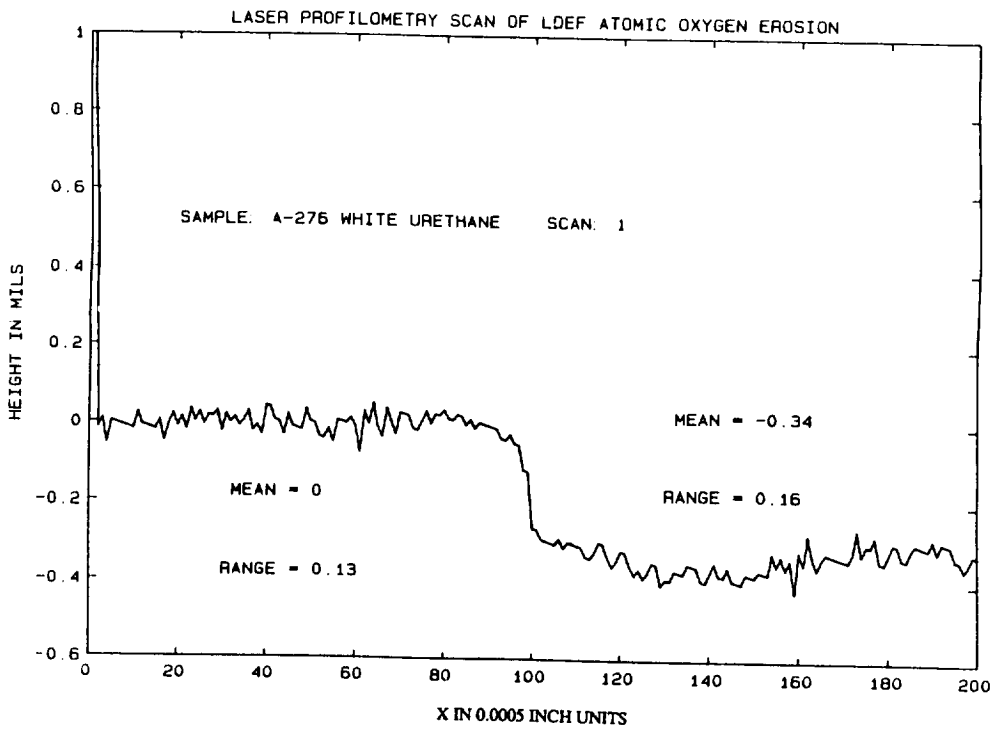Figure 7. Auger profile of tan area on the black chromium plated solar absorber panel.

Figure 8. Laser profilometry of A276 white paint on tray D9 at a protected/unprotected interface towards row 10.
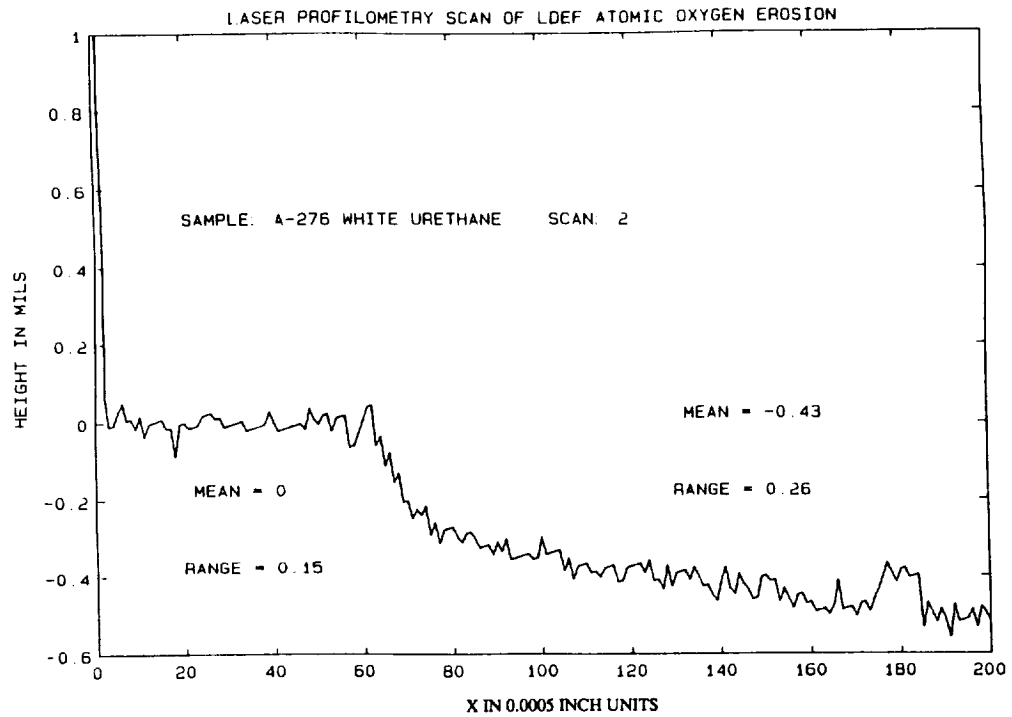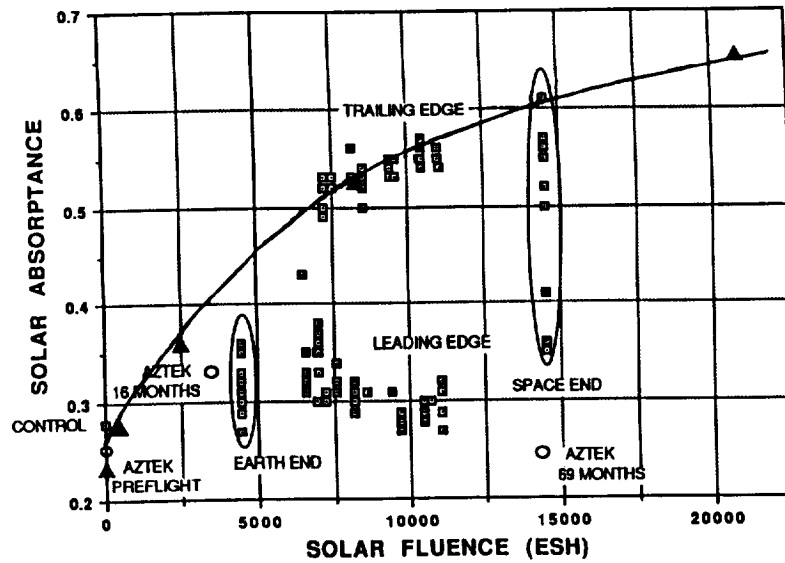
Figure 9. Laser profilometry of A276 white paint on tray D9 at a protected/unprotected interface towards row 8.

▲ 40 keV Electron + Protons		
Fluence (per cm²)	Scaled ESH	Absorptance
0	0	0.23
1 x 10¹⁴	420	0.27
6 x 10¹⁴	2500	0.36
2 x 10¹⁵	8300	0.52
5 x 10¹⁵	20800	0.66

Figure 10. Comparison of LDEF results with ground-based radiation test result from Boeing CRETC for A276 white paint.