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ANODIZED ALUMINUM ON LDEF*

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SUMMARY

A compilation of reported analyses and results obtained for anodized aluminum flown on the Long Duration Exposure Facility (LDEF) has been prepared. Chromic acid, sulfuric acid, and dyed sulfuric acid anodized surfaces were exposed to the space environment. The vast majority of the anodized surface on LDEF was chromic acid anodize because of its selection as a thermal control coating for use on the spacecraft primary structure, trays, tray clamps, and space end thermal covers. Reports indicate that the chromic acid anodize was stable in solar absorptance and thermal emittance, but that contamination effects caused increases in absorptance on surfaces exposed to low atomic oxygen fluences. There were some discrepancies, however, in that some chromic acid anodized specimens exhibited significant increases in absorptance. Sulfuric acid anodized surfaces also appeared stable, although very little surface area was available for evaluation. One type of dyed sulfuric acid anodize was assessed as an optical baffle coating and was observed to have improved infrared absorptance characteristics with exposure on LDEF.

INTRODUCTION

The anodize process is an electrolytic oxidation of metal, essentially a controlled corrosion process, which yields a uniform and adherent oxide coating. It is typically used in the aerospace industry for corrosion protection, wear resistance, and/or as a base for subsequent organic finishes. In the context of this paper, however, anodized aluminum is utilized with regard to its ability to function as a thermal control coating for spacecraft use. In this capacity, anodized aluminum offers significant advantages including terrestrial durability, light weight, processing simplicity, and some tailorability of optical properties. The LDEF mission has provided a basis for evaluating the impact of the space environment on the ability of anodized aluminum to act as a predictable thermal control coating.

Aluminum anodizing as a process begins with a thorough cleaning of the aluminum part after all machining and heat treatment has been completed. The aluminum is then deoxidized to provide a uniform surface for anodizing. Sometimes a chemical polishing, or a bright dip, is performed at this point to establish a high initial reflectivity for the surface. Next, the part is placed in an electrolyte, and an electrical potential is established with the aluminum part as the anode. An oxide layer forms from the surface aluminum with a density and thickness principally controlled by the electrolyte composition and temperature, and by the voltage and time (total current) specified for the particular anodizing process.

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This as-anodized surface is highly porous on a submicron level. Finally, the electrolytically formed aluminum oxide coating is hydrated or sealed to close the porosity, bringing the surface to an equilibrium which is stable in the terrestrial environment and protective to the substrate material. Coloration of the anodize can be achieved through the occlusion of dyes in the pore structure prior to hydration or sealing.

Three types of anodized aluminum were flown on LDEF, for which results have been published. The types are chromic acid anodize, sulfuric acid anodize, and dyed sulfuric acid anodize. This paper is a compilation of results for these finishes.

RESULTS AND DISCUSSION

Chromic Acid Anodize

Chromic acid anodize was used as part of the passive thermal management system for LDEF. The anodize process used for LDEF structures was actually a modification of the standard chromic acid anodize process, as specified by MIL-STD-8625, Anodic Coatings for Aluminum and Aluminum Alloys, Type I. The modified process used for LDEF was developed by NASA Langley Research Center (LaRC), and permits tailoring of solar absorptance and thermal emittance through the selection and control of anodizing voltage and time (ref. 1). LDEF structural components were constructed of 6061 aluminum alloy and were anodized using the modified chromic acid process to achieve an average absorptance/emittance ratio of 0.32/0.16.

Postflight optical property measurements for LDEF longerons, intercostals, and thermal panels have been reported (ref. 2). Average emissivity readings taken on exposed LDEF structures indicated that there were no measurable changes when compared to preflight conditions ($\varepsilon = 0.15 \pm 0.03$), regardless of location. However, surfaces protected from atomic oxygen (AO) or ultraviolet (UV) radiation by overlapping structures exhibited a slight increase in average emissivity ($e = 0.18 \pm 0.04$). The cause of the slight emissivity increase for unexposed surfaces has not been determined.

Solar absorptance measurements for space-end thermal panels indicated an average increase of 0.03 from preflight conditions. Absorptance measurements made for intercostals and longerons indicated a more complex situation, and have been plotted versus row location in Figure 1. Data in Figure 1 for intercostals are located on the row numbers, and longerons data are between row numbers. For structures subjected to significant AO fluences (leading edge row locations 6.5 through 11.5), measurements indicated absorptances comparable to those made preflight ($\Delta\alpha < 0.02$). The longerons contributed most to the differences observed between preflight and postflight solar absorptance measurements on the leading edge structures. Structures subjected to low AO fluences (trailing edge row locations 12 and 0.5 through 6), however, exhibited significant increases in absorptance ($\Delta\alpha = 0.07$). Some indication of trends in the preflight solar absorptance measurements were still apparent in the postflight measurements on trailing edge row structures, such as was observed on the longeron between rows 2 and 3.

In an attempt to further investigate the cause(s) of absorptance changes for chromic acid anodize on the LDEF structure, solar absorptance has also been plotted as functions of UV radiation exposure and AO fluence in Figures 2 and 3, respectively. The UV exposure and AO fluence numbers were taken from the LDEF environmental exposure models (ref. 3). Figure 2 indicated that the influence of UV exposure on solar absorptance was not strong. However, Figure 3 indicated that AO fluence does have a significant effect on solar absorptance, but that the effect was not a gradual one even when represented on a log-scale. Once a "threshold" AO fluence was reached, the average solar absorptance rapidly returned to preflight values. Recognizing this strong effect of AO above the threshold fluence, solar absorptance versus UV exposure was replotted using only data from structures which received an AO fluence below the threshold ($<10^{20}$ atoms/cm^2), as shown in Figure 4. A weak effect of UV exposure on solar absorptance was revealed, indicating an absorptance increase of approximately 0.008 per 1,000 equivalent Sun hours (ESH) of UV exposure.

Thermal control properties were also measured for the tray clamps used to hold experiment trays to the LDEF framework. Reported results (ref. 4) have been summarized in Table 1. No significant changes in emissivity were observed for the exposed surfaces of tray clamps, as compared to preflight data. Tray clamps exposed to fluences of atomic oxygen greater than 10^{20} atoms/cm^2, reported in Table 1 as ram side surfaces, did not indicate significant changes in solar absorptance. Tray clamps with less than the threshold AO fluence (wake side, Earth end, and space end surfaces) did have measurable but slight increases in average absorptance ($\Delta\alpha = 0.03$). Note that averages for flight tray clamps, regardless of their exposure conditions, exhibited optical properties closer to preflight measurements than did tray clamps held in uncontrolled storage during the LDEF mission. Anodize thickness measurements were also made, indicating that an emissivity of 0.16 corresponds to an anodize layer thickness of between 0.4 and 0.6 µm (about 0.00002 inch).

Table 1. Solar absorptance and thermal emittance measurement averages for 6061 aluminum tray clamps (including standard deviations, σ).

Measurements on Flight Tray Clamps						Measurements on Unused Clamps
Protected Surfaces	Ram Side Surfaces	Wake Side Surfaces	Space End Surfaces	Earth End Surfaces	Preflight (ref. 1)	
$\alpha = 0.34$ $[\sigma = 0.01]$	$\alpha = 0.33$ $[\sigma = 0.01]$	$\alpha = 0.35$ $[\sigma = 0.02]$	$\alpha = 0.35$ $[\sigma = 0.02]$	$\alpha = 0.35$ $[\sigma = 0.01]$	$\alpha = 0.32$	$\alpha = 0.36$
$\varepsilon = 0.16$ $[\sigma = 0.01]$	$\varepsilon = 0.15$ $[\sigma = 0.01]$	$\varepsilon = 0.15$ $[\sigma = 0.01]$	$\varepsilon = 0.16$ $[\sigma = 0.02]$	$\varepsilon = 0.17$ $[\sigma = 0.01]$	$\varepsilon = 0.16$ $[\sigma = 0.01]$	$\varepsilon = 0.18$ $[\sigma = 0.01]$
$\alpha/\varepsilon = 2.1$	$\alpha/\varepsilon = 2.2$	$\alpha/\varepsilon = 2.3$	$\alpha/\varepsilon = 2.2$	$\alpha/\varepsilon = 2.1$	$\alpha/\varepsilon = 2.0$	$\alpha/\varepsilon = 2.0$

Chromic acid anodized flight specimens of 6061 aluminum were flown as part of LDEF experiment S0010 (refs. 5, 6). The thermo-optical property measurements, shown in Table 2, indicate that the chromic acid anodize specimens were not significantly affected by either short-term (10 months, 1,600 ESH UV, and $<10^{17}$ AO atoms/cm^2) or long-term (5.8 years, 11,200 ESH UV and 9×10^{21} AO atoms/cm^2) exposure.

Another example of chromic acid anodize involved the surface of environment exposure control canisters (EECC) used on several LDEF experiments. Measurements of thermo-optical properties on the surfaces of these 6061 aluminum canisters have been reported for Experiment S1002 (ref. 7) and obtained from Experiment M0003 investigators (M. Meshishnek), shown in Table 3. The results in Table 3 are consistent with those observed for chromic acid anodize on the other LDEF structures.

Emissivity was not affected by the LDEF exposure conditions. Solar absorptance was not significantly affected in high AO fluence regions but increased by approximately 0.07 on low AO fluence surfaces.

Table 2. Solar absorptance and thermal emittance measurements for 6061 aluminum chromic acid anodize test specimens on LDEF experiment S0010 (ref. 5).

Coating	Preflight		10-Month Exposure		5.8-Year Exposure	
	α	ε	α	ε	α	ε
Thin chromic acid anodize	0.295	0.16	0.299	0.17	–	–
	0.288	0.18	–	–	0.296	0.19
Medium chromic acid anodize	0.292	0.43	0.287	0.43	–	–
	0.396	0.45	–	–	0.311	0.46
Thick chromic acid anodize	0.330	0.71	0.337	0.71	–	–
	0.341	0.75	–	–	0.354	0.75

Table 3. Solar absorptance and thermal emittance of 6061 aluminum EECC chromic acid anodized surfaces.

Experiment Number	Tray Location	UV (ESH)	AO (atoms/cm^2)	Preflight		Postflight	
				α	ε	α	ε
S1002	E3	11,100	10^{17}	0.29	0.19	0.36	0.20
M0003	D4	10,500	10^{5}	–	–	0.40	–
	D8	9,400	7×10^{21}	–	–	0.32	–

Results from Experiment S0069 (ref. 8) were not consistent with other results reported here for chromic acid anodized 6061 aluminum surfaces. Two specimens of chromic acid anodized 6061 aluminum were flown on tray A9, but when battery power failed for this active experiment (due to the unplanned extension of the LDEF mission) one specimen (C61) was exposed for the entire mission, and the other specimen (C63) was exposed for only the initial 19 months. The solar absorptance data for these two specimens were measured in situ, and are shown in Figure 5 as a function of estimated UV exposure. The last measurement for specimen C63 was actually made postflight, but is plotted on Figure 5 at the exposure it would have received for 19 months. These measurements indicated that the S0069 specimens degraded (increased) in solar absorptance at a rate of 0.04 per 1,000 ESH of UV exposure. The solar absorptance of specimen C61, however, recovered significantly due to the AO fluence received in the latter stages of the LDEF mission (from 0.50 to 0.47). The preflight and postflight emissivity for both of these two specimens was 0.84, unchanged with exposure as has been observed with other anodized surfaces. The emissivity measured for the two specimens on Experiment S0069 was surprisingly high for chromic acid anodized aluminum. The maximum emissivity for chromic acid anodize has been 0.70 to 0.75.

Chromic acid anodized 2024 aluminum alloy was also flown on LDEF. Investigators for Experiment A0034 used this material and finish combination for top cover plates (ref. 9). The thermal control coatings evaluated in Experiment A0138-6 (ref. 10) included a test specimen of chromic acid anodized 2024 aluminum (specific designation was alloy AU4G1, specimen E7). Results of absorptance

Table 4. Solar absorptance and thermal emittance of 2024 aluminum chromic acid anodized surfaces.

Experiment Number	Tray Location	UV (ESH)	AO (atoms/cm^2)	Unexposed Back		Exposed Front	
				α	ε	α	ε
A0034	C9	11,200	9×10^{21}	0.42	0.15	0.38	0.13
	C3	11,100	10^{17}	0.45	0.14	0.47	0.13
				Preflight		Postflight	
A0138-6	B3	1,582	negligible	0.48	0.34	0.54	0.34

and emittance measurements are shown in Table 4. The results for Experiment A0034 are somewhat difficult to interpret without preflight data. However, it was apparent to the investigators that a high AO fluence "cleaned" the tray C9 exposed cover plate surface. If it is assumed that this cleaned surface mimics the original absorptance of that surface, as has been observed for other LDEF chromic acid anodized surfaces, then that absorptance could be used as an indication of the cover plate preflight condition. Using this assumption, the cover plate for tray C3, with a low AO fluence, exhibited an absorptance increase of 0.09. Such an absorptance degradation is slightly higher than but comparable to that observed for the anodize on LDEF structures.

The test specimen flown on Experiment A0138-6 indicated significant degradation in solar absorptance considering its limited exposure (see Table 4). Since this test specimen was in an open canister during the initial 10 months of the LDEF mission, it received limited UV radiation and a negligible AO fluence (estimated at $<10^3$ atoms/cm^2). The absorptance increase was measured as $\Delta\alpha = 0.06$, or 0.04 per 1,000 ESH. This degradation rate was comparable to that observed for specimens on Experiment S0069.

As a comparison to LDEF flight data, ground-based testing data for chromic acid anodize (ref. 11) has been included here. Figure 6 shows how solar absorptance was affected by UV exposure for a chromic acid anodized 1145 aluminum alloy foil. An increase in solar absorptance of from 0.32 to 0.34 was observed in the initial 500 ESH of exposure. The test specimen then held at a constant solar absorptance of 0.34 for the next 4,500 ESH exposure tested. The thermal emittance of the specimen from this test was measured as 0.67, indicating a relatively thick oxide layer.

Sulfuric Acid Anodize

Experiment S1002 included both experimental and nonexperimental surfaces finished with sulfuric acid anodize (ref. 7). The experimental surface was an optical solar reflector (OSR), described as a 5-µm sulfuric acid anodize coating on an aluminum substrate. The OSR received a controlled environmental exposure due to its position in an EECC, amounting to 1,440 ESH of UV exposure and negligible atomic oxygen. Thermal control characteristics changes were minimal, with a postflight solar absorptance of 0.09 ($\Delta\alpha = 0.01$) and emissivity of 0.79 ($\Delta\varepsilon = 0.01$). The calorimeter support of Experiment S1002 was also sulfuric acid anodized and received the full mission experimental environmental exposure for tray E3 (11,100 ESH UV exposure and 10^{17} AO atoms/cm^2). Emissivity on this nonexperimental surface was 0.76, whether measured on exposed or protected areas. Solar absorptance had increased slightly from 0.38 to 0.40 when moving from protected to exposed surfaces. The investigator cited contamination as the cause of the absorptance increase, with contamination enhanced by the coating porosity.

A disk of 6061 aluminum was sulfuric acid anodized for exposure on Experiment M0003 (ref. 12). The specimen was anodized to specification coating weight requirements of 1,500 to 2,000 mg/ft^2, and it received a chromate seal. After receiving 11,100 ESH UV exposure and 10^{17} atoms/cm^2 AO fluence, the postflight solar absorptance had increased only slightly, from 0.40 to 0.42. However, emissivity apparently increased significantly, from 0.75 to 0.84. This is the only example of a significant emissivity change for anodize that has been reported for LDEF. However, based on the established coating weight requirement, the preflight emissivity measurement is considered questionable, and it is suspected that there was no actual change in emissivity for this sulfuric acid anodized test specimen.

Dyed Sulfuric Acid Anodizing

Only one example of a dyed anodize coating has been reported from LDEF. Experiment S0050 involved a number of optical baffle coatings for low infrared reflectance (ref. 13). One of the coatings evaluated was a sample described as "Martin Black Anodize." This coating was a sulfuric acid anodize which had been permeated with a complex organic dye, and sealed in hot water. (Martin Black Anodize is prepared by Martin Marietta Astronautics Group.) Analysis of the black anodize coating was conducted after exposure to approximately 4,000 ESH of UV radiation and minimal atomic oxygen, due to location and test substrate orientation for experiment S0050. Postflight results indicated that the black anodize had increased its absorptance of wavelengths less than 150 microns. In this application, such an effect is a desirable consequence of space environmental exposure. The black anodize was, of the materials tested, alone in exhibiting this effect. Experiment investigators have postulated that this effect was the result of an increased density of absorption sites, formed as a result of vacuum and UV exposure.

CONCLUSIONS

For dyed anodize, there has been only one reported example from LDEF. The Martin Black Anodize improved in infrared absorptance with vacuum and moderate UV radiation exposure, but low AO fluence. The coating was evaluated for use as an optical baffle finish.

Performance results from sulfuric acid anodize looked very good. The available test surface area was limited, and no results were obtained for high AO fluence environment. However, the specimens flown indicated good solar absorptance stability to the UV radiation environment. Emissivity is considered stable. Although one specimen indicated a significant emissivity increase with exposure, the cause is thought to be preflight measurement error, based on the specified coating weight (thickness) of the oxide film.

A very large surface area of chromic acid anodize was exposed to all of the environmental conditions available from the LDEF mission. When considering the majority of measurements made from available surfaces, chromic acid anodize is stable in both solar absorptance and thermal emittance. Over 500 measurements have been made on structures, EECC's, and cover plates, with minimal changes observed in absorptance for areas of high AO fluence. The solar absorptance changes observed for low AO fluence areas have been attributed to contamination processes occurring early in the LDEF mission. Emissivity on structural components was low (~0.2) and not significantly changed by the environment.

Inconsistencies have been observed, however, for chromic acid anodize. Test specimens having higher emissivities, or thicker anodize coatings, have not indicated any changes in thermal emittance with exposure. But solar absorptance for one set of specimens indicated excellent stability over a broad range of exposure conditions, whereas another set of specimens indicated a trend in solar absorptance degradation increasing at a rate of about 0.04 per 1,000 ESH. A failure analysis on the degraded chromic acid anodize specimens is needed to bring higher confidence to the assertion based on measurements from the vast majority of surface evaluated, that chromic acid anodize is stable in the low Earth orbital environment.

The central issue affecting absorptance stability for chromic acid anodize is likely one of contamination. Several authors have indicated that solar absorptance increase on anodize was associated with contamination. It was also apparent that AO fluences above the "threshold" of 10^{20} atoms/cm^2 reversed or removed the absorptance degradation effects. The primary concern does not appear to be one of inherent instability in the oxide produced through chromic acid anodize, but that the porosity of the anodize could act as a "sink" for molecular contamination.

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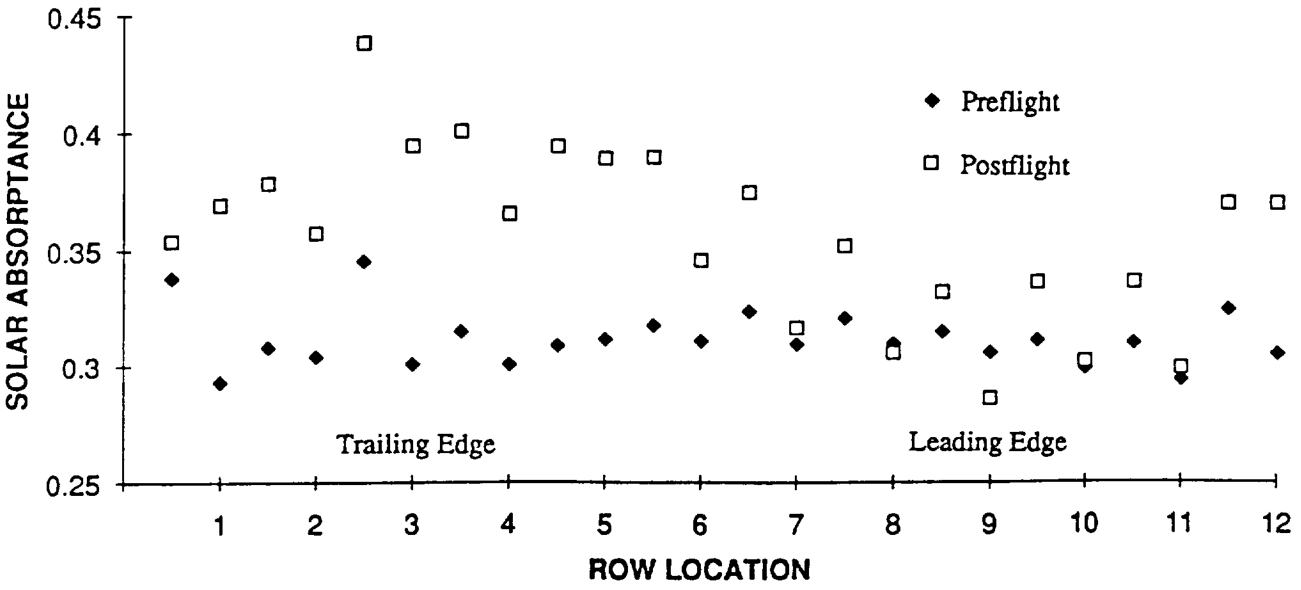

Figure 1. LDEF chromic acid anodize on longerons and intercostals, preflight and postflight absorptance versus row location.

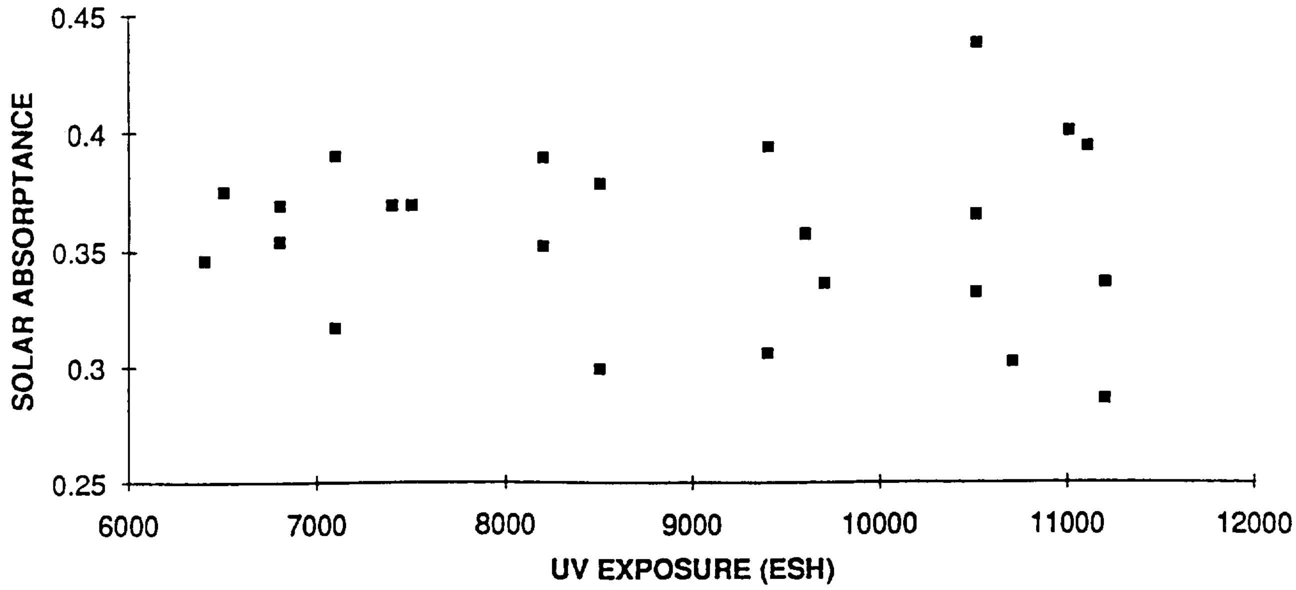

Figure 2. LDEF chromic acid anodize on longerons and intercostals, absorptance versus UV exposure.

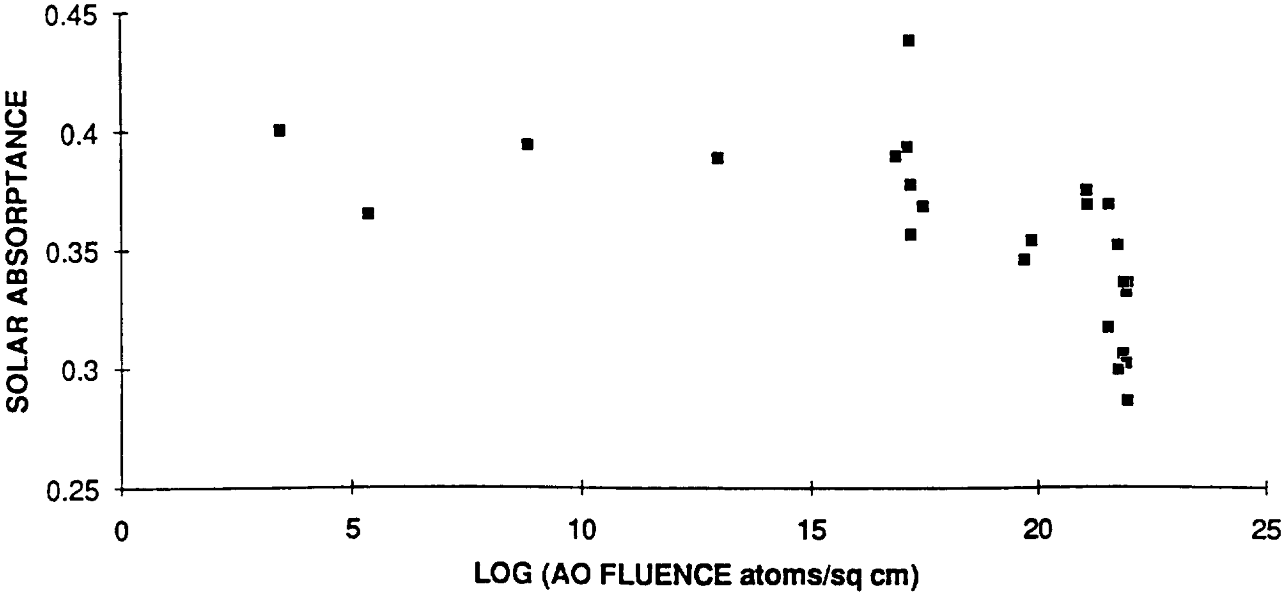

Figure 3. LDEF chromic acid anodize on longerons and intercostals, absorptance versus AO fluence.

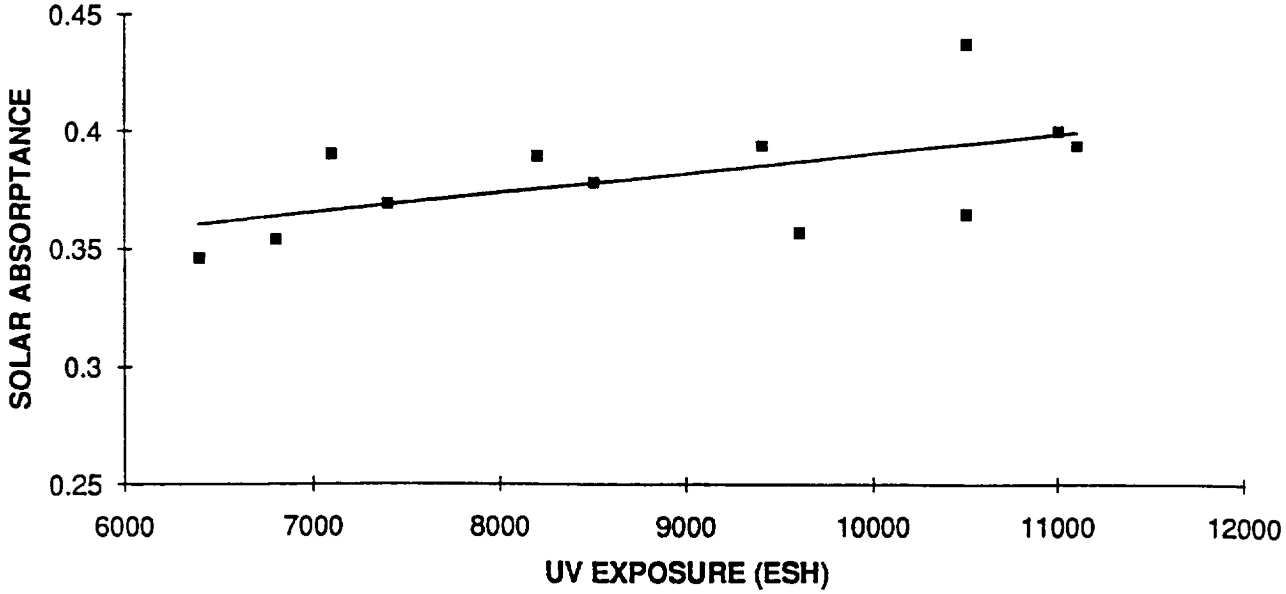

Figure 4. LDEF chromic acid anodize on low AO exposure longerons and intercostals, absorptance versus UV exposure.

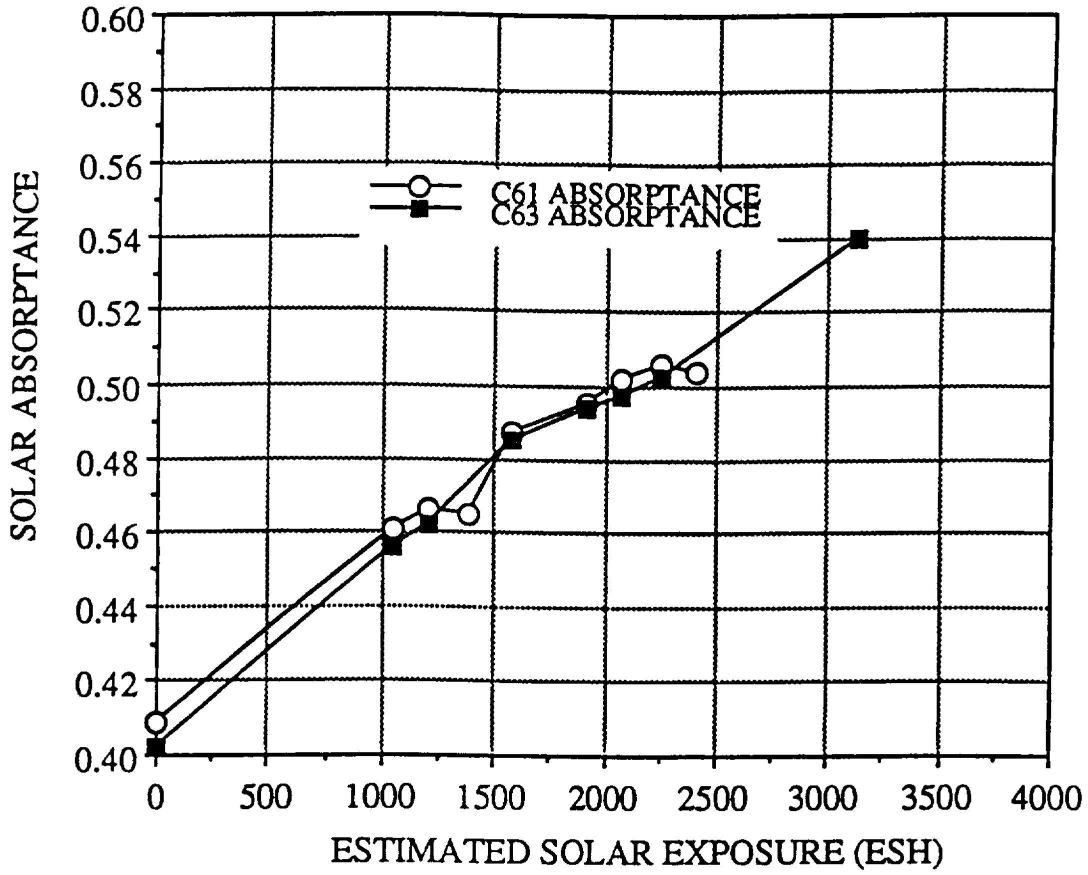

Figure 5. Experiment S0069 chromic acid anodize on 6061 aluminum, absorptance versus UV exposure.

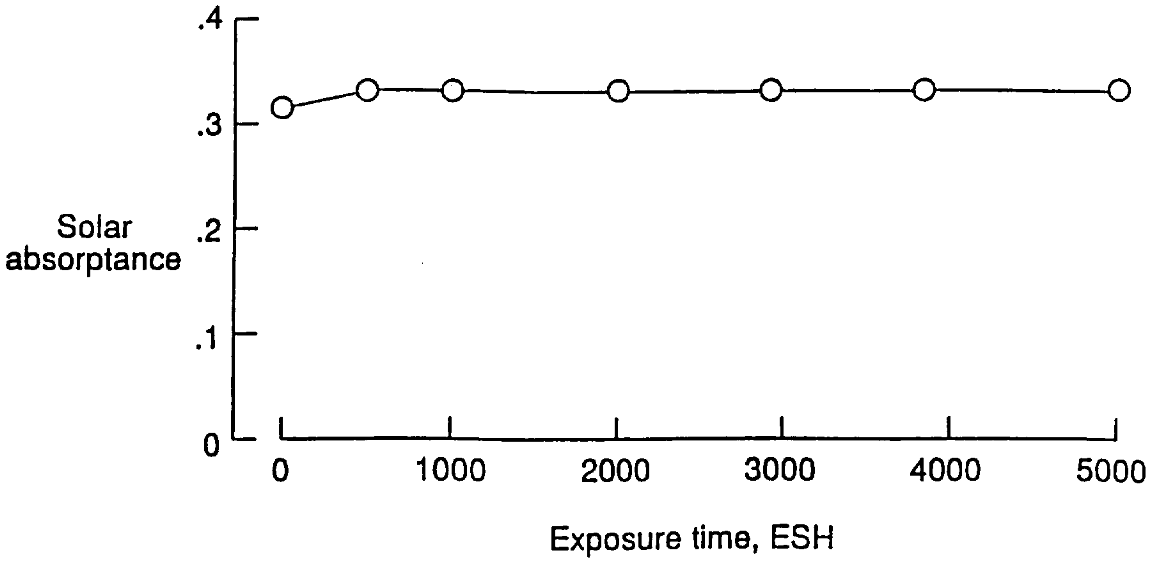

Figure 6. Chromic acid anodized 1145 aluminum foil, effects of groundbased UV exposure on absorptance (Ref. 11).