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COMPARISON OF SULFURIC AND OXALIC ACID ANODIZING FOR PREPARATION OF THERMAL CONTROL COATINGS FOR SPACECRAFT*

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ABSTRACT

The development of thermal control surfaces, which maintain stable solar absorptivity and infrared emissivity over long periods, is challenging due to the severe conditions in low-Earth orbit (LEO). These conditions include ultraviolet radiation, atomic oxygen, and thermal cycling as the spacecraft passes into and out of the Earth's shadow. Some candidate coatings are second-surface silver-coated Teflon; second-surface, silvered optical solar reflectors made of glass or quartz; and anodized aluminum. We have evaluated sulfuric acid anodized and oxalic acid anodized aluminum under simulated LEO conditions. Oxalic acid anodizing shows promise of greater stability in LEO over long missions, such as the 30 years planned for the Space Station. Sulfuric acid anodizing; however, shows lower solar absorptivity.

INTRODUCTION

Thermal control systems are needed on spacecraft to maintain temperatures in the range required for effective operation. These systems have a surface which is exposed to space and has a range of acceptable values for solar absorptivity (α) and for infrared emissivity (ε). Usually, the surfaces are chosen to have the lowest possible absorptivity and the highest possible emissivity, for the minimum α/ε ratio. One material used for these surfaces is FEP Teflon film with a silver-coated second surface. However, samples of this material which were returned from the Solar Max satellite after repair showed significant degradation after only four years.[1] Although the degradation may be due to exposure conditions and temperatures that were more severe than those expected, there is concern that this material will degrade during the extremely long periods of time planned for spacecraft; such as the Space Station. Another surface used on satellites is thin glass or quartz with a second-surface silver coating. These surfaces show good stability; however, they are expensive to make and attach to a radiator or other structures. There is also insufficient data on their stability or the stability of the adhesives used to attach them for many years in orbit.

Anodizing, which is the process of electrochemically forming a coating of aluminum oxide on an aluminum surface, has been investigated for more than 20 years for thermal control coatings for low α, high ε applications[2]. Large areas can be anodized in a relatively short period of time; the surface is much harder and more resistant to damage than other thermal control coatings. The three most common types of anodizing are produced using chromic, phosphoric, and sulfuric acid. Of these, only sulfuric acid anodizing has a sufficiently low α to be a candidate for spacecraft radiators. Depending on the alloy and the anodizing process conditions, α can be as low as 0.1, and ε can be as high as 0.9. However, sulfuric acid anodizing is not stable to the ultraviolet radiation in space and the α tends to increase with time in orbit, possibly due to the formation of defects in the lattice which increase scattering of the solar radiation[2]. One theory for the susceptibility of sulfuric acid anodizing to ultraviolet radiation is that it is sensitized by sulfur or sulfate anions occluded in the

lattice. Sulfuric acid anodized coating contains about 13% to 18% of sulfate $(Al_2(SO_4)_3)$.

We investigated oxalic acid for thermal control surfaces because there are no inorganic ions occluded in the aluminum oxide that may sensitize the anodizing to ultraviolet radiation. Although oxalic acid is not commonly used in the United States, it is more popular in Japan where it was first developed. Oxalic acid anodized coating has about 3% of oxalic acid in the form of aluminum oxalate[3] $(Al_2(C_2O_4)_3$, indicating that it may be less susceptible to changes due to UV. Also, faying surface corrosion of anodized components due to oxalic acid residues is not a problem, in contrast to chromic and sulfuric acid residues, since neutralization with dilute ammonia or sodium bicarbonate is adequate to avoid corrosion.

EXPERIMENTAL PROCEDURE

SAMPLE PREPARATION

Previously anodized 5657 aluminum/magnesium alloy with the trade name Coilzak was selected as our test material since bare 5657 alloy was unavailable at the time this work was performed. This alloy was first studied for spacecraft thermal control coatings by D. Duffy[4]. Coilzak is extensively used in the automotive industry; it is preanodized by Alcoa, and has a high specular reflectivity. The test samples were fabricated from a 0.081 cm (0.032 in.) thick Coilzak sheet into 8 x 25 cm specimens.

In the anodizing sequence the test specimens were stripped with a phosphoric/chromic acid stripper to remove the preanodized coating (Figure 1). The test specimens were bright dipped in a phosphoric/nitric acid solution at temperatures from $95^{\circ}C$ to $100^{\circ}C$ for 45 seconds. After anodizing, the test specimen was wiped with a clean cloth to remove smut. (Smut is a thin layer of unwanted material formed during processing.)

We performed the anodizing process in the Chemistry Laboratory pilot process line at our facility. Anodizing was accomplished in a temperature controlled lead tank with a volume of 11 L. Power was supplied by a Trygon 40-volt, 8-amp power source using the lead tank as the cathode.

ANODIZING PARAMETERS

We performed a series of experiments to determine the optimum electrolyte concentration, current density, anodizing time, and bath temperature for oxalic acid anodizing. Our preliminary results indicate that an electrolyte concentration of 15% oxalic acid at a current density of 10 amperes per square foot (A/sq ft) yields the most suitable anodic coating. To produce the best α/ϵ ratio of 0.20 for oxalic acid anodizing, we first selected a $50^{\circ}C$ electrolyte temperature (Figure 2). However, Taber abrasion and ultraviolet test results showed that the coating prepared at this temperature is mechanically weak and unstable to ultraviolet radiation in vacuum. At $0^{\circ}C$ to $20^{\circ}C$ the coatings exhibit good abrasion resistance but poor optical properties. The best combination of results is obtained at $30^{\circ}C$. These results show that higher electrolyte temperatures yield better optical properties (lower α/ϵ ratio) but softer coatings.

The optical properties of coatings prepared at different current densities and anodizing times at $30^{\circ}C$ show that sulfuric acid anodized aluminum yields a better α/ϵ ratio (0.20) than that of oxalic acid anodizing (0.25) and its emissivity increases more rapidly with increasing coating thickness.

ULTRAVIOLET RADIATION EXPOSURE

Test samples of candidate coatings were subjected to an ultraviolet flux equivalent to two and three solar constants intensity at NASA Langley Research Center (NASA-LaRC) and the TRW Thermophysical Laboratory, respectively.

At NASA-LaRC, a modular ultraviolet exposure system consisting of six high vacuum chambers surrounding a 1 KW xenon arc lamp source was used for ultraviolet exposure of anodized aluminum specimens over the wavelength region of 0.18 to 0.40 microns. Quartz optics were used to transmit the ultraviolet radiation incident on the 1-in. square specimens in these individual vacuum chambers. Typical vacuum in each chamber was 1×10^{-8} torr. Each test specimen was mounted on a water cooled plate and the test temperature was less than $43^{\circ}C$.

Reflectance was measured in-situ using a Beckman DK2A spectrophotometer with an integrating sphere reflectometer. Measurements were made over a wavelength range of 0.25 to 2.5 microns. Reflectance data was recorded by a computer at 0.015 micron intervals and integrated over an air mass 0 solar spectrum to obtain the solar absorptance. Values of normal emittance at room temperature were determined ex-situ using a Gier-Dunkle Instrument DB-100 Emissometer[5].

At TRW, a similar ultraviolet exposure system was employed for exposure of anodized aluminum specimens. A 5 KW xenon arc lamp was used as the ultraviolet radiation source over the wavelength region of 0.18 to 0.40 microns. The 1-in. square specimens were mounted on a water cooled plate which was then enclosed in a quartz tube and pumped down to a vacuum of 1×10^{-6} torr. The exposure temperature was approximately $66^{\circ}C$.

The solar absorptance and normal emittance at room temperature of the test specimens were measured using a technique similar to that used at NASA-LaRC. Spectral directional reflectance was measured in-situ using a Beckman DK2A spectrophotometer with an Edwards type integrating sphere reflectometer. Measurements were made over a wavelength region from 0.28 to 2.5 microns. Solar absorptance was determined by first finding the average reflectance of the specimen at a number of wavelength bands. An overall average solar reflectance was then calculated; subtracting this value from unity gives solar absorptance for an opaque specimen. The normal emittances at room temperature were determined using a Gier-Dunkle Instrument Model DB-100 Infrared Reflectometer.

RESULTS AND DISCUSSION

ULTRAVIOLET RADIATION

After 1000 equivalent sun hours (ESH) exposure at two solar constants at NASA-LaRC, both oxalic and sulfuric acid anodized aluminum samples developed a yellowish color with increased solar absorptivity. In all cases, emittance was unaffected by ultraviolet radiation.

Oxalic acid anodized samples produced at 50°C electrolyte temperature degraded significantly compared to those produced at 30°C (Table 1). However, the oxalic acid anodized coatings produced at the lower temperature were more stable to the ultraviolet radiation than the control sulfuric acid anodized samples produced at the same temperature. For example, the change in solar absorptance ($\Delta\alpha$) of the oxalic acid anodized sample is 0.023 after 1000 ESH, while the sulfuric acid anodized sample with a similar coating thickness exhibited $\Delta\alpha$ of 0.063. The change in absorptance as a function of exposure hours at two solar constants of oxalic acid anodized aluminum (Figure 3) indicates that the degradation increased gradually from 300 to 1000 ESH. Long-term exposure (5000 ESH) testing is needed to determine whether the degradation will be stable with time.

We also subjected the anodized aluminum to ultraviolet radiation at three solar constants at TRW Thermophysical Laboratory to determine if there is a direct correlation between different levels of accelerated ultraviolet testing. After ultraviolet exposure at three solar constants for 1000 ESH, oxalic acid anodizing produced at 50°C showed severe degradation similar to that at two solar constants (at NASA-LaRC). Both oxalic and sulfuric acid anodized samples produced at 30°C exhibited a similar change in absorptance (0.04) (Table 2). However, both of the sample surfaces cracked after 1000 ESH. The cracks on the oxalic acid anodizing radiated from several edge locations and appeared to be caused by mechanical handling. The sulfuric acid anodizing had many uniformly distributed short cracks, indicating a different cause. Possibly differential expansion during ultraviolet exposure combined with the residual stress in the anodize layer to produce these cracks. It was hypothesized that the exposure temperature was much higher than the anticipated 27°C. Thus, identical samples were resubjected to ultraviolet exposure. The exposure temperature was measured by attaching a thermocouple directly to the exposure surface. It was observed that at only two solar constants the test temperature was elevated to 43°C. To avoid damaging the anodized samples, the ultraviolet exposure was conducted at two solar constants for 1000 ESH. One interesting note was that the sulfuric acid anodized sample started to craze under vacuum prior to ultraviolet exposure. The oxalic acid anodized crazed after 500 ESH. However, the change in absorptance of oxalic acid anodizing after 1000 ESH (0.03) was significantly

less than that of sulfuric acid anodizing (0.08)(Table 3). Thus, ultraviolet test results obtained at two solar constants at both test facilities (TRW and NASA-LaRC) indicate that oxalic acid anodizing is more stable to ultraviolet radiation than sulfuric acid anodizing.

Further investigation is being conducted to solve the crazing problem which occurs on the anodized samples during ultraviolet exposure at TRW.

We also investigated the phenomenon of "bleaching", which has been observed with white paints[5,6], to determine if there is a lowering of absorptance for clear anodized aluminum on exposure to atmospheric oxygen after ultraviolet exposure. Solar absorptance was measured both ex-situ and in-situ. Although the mechanism of bleaching has not been fully explained, a likely explanation is that color centers formed within the film under ultraviolet radiation are partly destroyed in the presence of oxygen in air. Our results showed that bleaching occurs and the ultraviolet degradation is reversed in both oxalic and sulfuric acid anodized coatings (Table 4). However, only a small portion of the solar absorptance gain is reversed, indicating that bleaching with molecular oxygen is not a feasible approach for reconditioning anodized coatings.

THERMAL CYCLING

The clear anodized aluminum samples were subjected to thermal cycling from -73°C to 38°C in a nitrogen environment. After 4000 cycles, neither oxalic nor sulfuric acid anodized coatings of various thicknesses (0.012 to 0.0203 cm) exhibited cracking or spalling and their emissivity remained unchanged.

SALT SPRAY CORROSION RESISTANCE

Both types of clear anodizing passed the salt spray testing, conducted under conditions specified in ASTM method B117-73, indicating that corrosion resistance satisfies Military Specification 8625, Anodizing of Aluminum Alloys. This also indicated that no corrosion problems would occur with either type through production, transportation, or prelaunch storage.

ABRASION RESISTANCE

Taber Abraser tests on oxalic and sulfuric acid anodized aluminum (Table 5) showed that oxalic acid anodizing produced at a low temperature (30°C) was somewhat more resistant to abrasion than sulfuric acid anodizing produced at the same temperature, and that the oxalic acid coating produced at 50°C eroded rapidly. These results are probably due to the porous structure of the anodic surface, as observed in the scanning electron micrographs (Figures 4 and 5).

SCANNING ELECTRON MICROSCOPY

Using scanning electron microscopy, we examined the surface morphology of the oxalic acid anodized coatings produced at 30°C and 50°C electrolyte temperatures (Figures 4 and 5). The surface produced at 50°C is significantly more porous than that produced at 30°C, indicating that more contaminants can be trapped inside the pores, lowering its ultraviolet stability.

We also examined the anodizing produced at 30°C by sulfuric acid, and by oxalic acid using the scanning electron microscope. No significant differences were observed.

CONCLUSION

The properties of the oxalic acid anodized thermal control coating prepared at 30°C are similar to the sulfuric acid anodized coating. Our current data obtained at two solar constants indicates that oxalic acid anodized coating exhibits significantly less degradation to ultraviolet radiation than sulfuric acid anodized coating. The most noteworthy observation is that our and Acurex' anodizing studies[4] show much less degradation than was reported in earlier work.[2] Further testing is in progress. Additional ultraviolet testing, which includes the shorter wavelength region (0.14 – 0.18 microns) and longer term exposure, is essential to ascertain the stability of both anodizing systems to be used as thermal control coatings in the LEO environment.

We will include selected oxalic and sulfuric acid anodized aluminum samples identical to those tested at our ground-based accelerated test facilities on

the FOIM-III (Evaluation of Oxygen Interactions with Materials-III) flight experiment[7]. The samples will be exposed for 40 hours in the LEO and will be retrieved for examination. These flight results will enable us to compare our simulated test results with those obtained in a real space environment.

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John M. Watcher attended California State University at Long Beach where he received his BS in chemistry in 1985. His interests include surface finishing such as anodizing, electroplating, chemical milling, and environmental effects related to the degradation of surface finishes. He is currently a technology engineer in the chemistry laboratories at McDonnell Douglas Astronautics Company – Huntington Beach. He is a member of the American Society of Testing Materials.

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Dudley L. O'Brien, after 25 years of service, has returned in a consulting capacity for the Materials, Processes, and Producibility department at McDonnell Douglas Astronautics Company - Huntington Beach. He joined the Air Force in 1943 and received his BS in chemistry and mathematics from Case Western Reserve University in 1950. His expertise in the field of metal finishing and processing include development of brighteners and low-temperature cleaners for electroplating, electropolishing, anodizing and chemical milling. His most recent interests are the development of thermal control chemical conversion coatings and electroplated coatings for aerospace applications and solar energy collectors.

Table 1. Effects of UV Exposure at Two Solar Constants for 1000 ESH on the Optical Properties of Oxalic and Sulfuric Acid Anodized Aluminum*

Anodized electrolyte (temperature)	Coating thickness (mil)	Solar absorptance (α)		
		Before exposure	After exposure	$\Delta\alpha$
Oxalic acid (50°C)	0.50	0.199	0.365	0.166
Oxalic acid (30°C)	0.65	0.250	0.249	0.024
Oxalic acid (35°C)	1.00	0.231	0.254	0.023
Sulfuric acid (30°C)	0.80	0.242	0.307	0.065

*Test performed at NASA-LaRC

Table 2. Effects of UV Exposure at Three Solar Constants on the Optical Properties of Oxalic Acid Anodized Aluminum*

Anodized electrolyte (temperature)	Coating thickness (mil)	Exposure time (ESH)	Solar absorptance (α)	
			After exposure	$\Delta\alpha$
Oxalic acid (50°C)	0.50	0	0.22	—
		100	0.28	0.06
		300	0.33	0.10
		500	0.36	0.13
		1000	0.38	0.16
Oxalic acid (30°C)	0.51	0	0.22	—
		300	0.25	0.03
		500	0.26	0.04
		700	0.26	0.04
		1000	0.26	0.04
Sulfuric acid (30°C)	0.55	0	0.17	—
		300	0.19	0.02
		500	0.21	0.04
		700	0.22	0.05
		1000	0.21	0.03

*Test performed at TRW Thermophysical Laboratory

Table 3. Effects of UV Exposure at Two Solar Constants on the Optical Properties of Oxalic Acid Anodized Aluminum*

Anodized electrolyte (temperature)	Coating thickness (mil)	Exposure time (ESH)	Solar absorptance (α)	
			After exposure	$\Delta\alpha$
Oxalic acid (30°C)	0.51	0	0.22	—
		250	0.25	0.03
		500	0.25	0.03
		1000	0.25	0.03
Sulfuric acid (30°C)	0.55	0	0.16	—
		250	0.22	0.06
		500	0.24	0.08
		1000	0.24	0.08

*Test performed at TRW Thermophysical Laboratory

Table 4. Effect of Bleaching on Oxalic and Sulfuric Acid Anodized Aluminum

Anodized electrolyte (temperature)	Exposure time (ESH)	Solar absorptance	
		In vacuum	In air
Oxalic acid (30°C)	0	0.225	0.228
	1000	0.249	0.240
Oxalic acid (50°C)	0	0.199	0.201
	1000	0.365	0.351
Surfuric acid (30°C)	0	0.242	0.238
	1000	0.307	0.291

Note: Exposing samples to air after they were exposed to UV radiation in vacuum

Table 5. Abrasion Resistance of Oxalic and Sulfuric Acid Anodized Aluminum

Wheel revolutions	Sulfuric acid anodized Al (30°C) weight loss (g)	Oxalic acid anodized Al (30°C) weight loss (g)	Oxalic acid anodized Al (50°C) weight loss (g)
0	0.0000	0.0000	0.0000
200	0.0015	0.0044	0.1542
450	0.0020	0.0050	0.1548
600	0.0030	0.0053	0.1624
3000	0.0174	0.0075	Bare metal

Note: Coating thickness of 0.40 mil; Teledyne Taber abraser conditions: load of 1 kg, CS17 wheel, 70 rpm
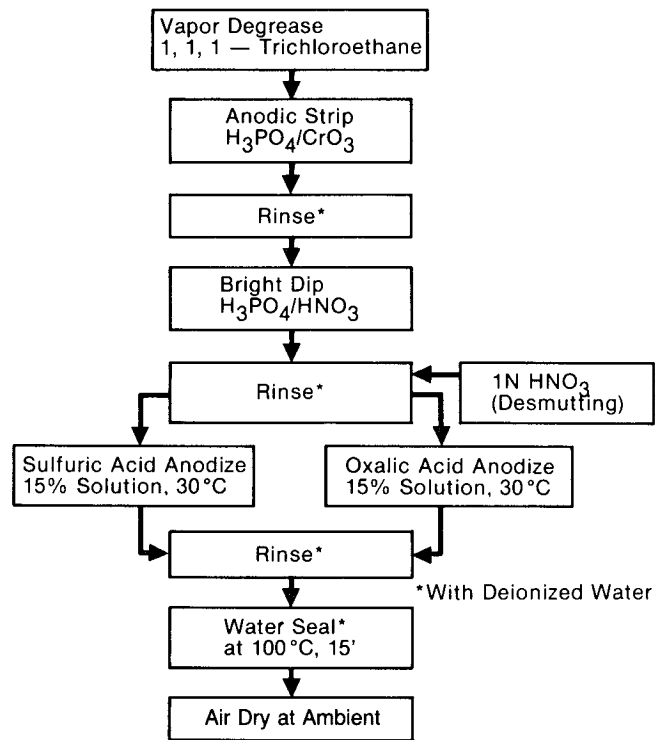
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┌─────────────────────────┐
│ Vapor Degrease          │
│ 1, 1, 1 — Trichloroethane│
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│    Anodic Strip         │
│    H3PO4/CrO3            │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│        Rinse*           │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│     Bright Dip          │
│     H3PO4/HNO3          │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐        ┌──────────────────┐
│        Rinse*           │◄───────│  1N HNO3         │
└─────────────────────────┘        │  (Desmutting)    │
                                   └──────────────────┘
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Anodic Strip
H_3PO_4/CrO_3

Bright Dip
H_3PO_4/HNO_3

Rinse*

1N HNO_3
(Desmutting)

Sulfuric Acid Anodize
15% Solution, 30 °C

Oxalic Acid Anodize
15% Solution, 30 °C

Rinse*

*With Deionized Water

Water Seal*
at 100 °C, 15'

Air Dry at Ambient
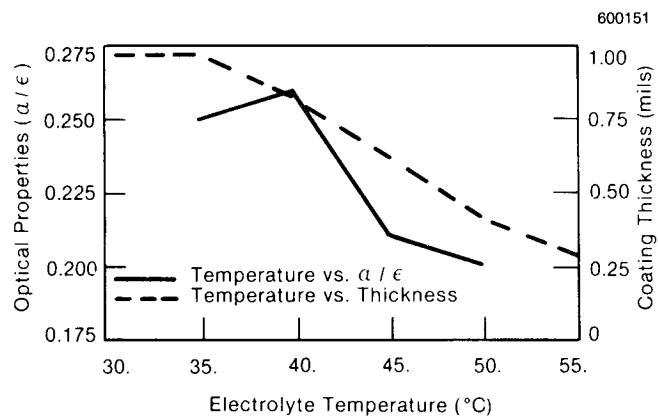
Figure 1. Flow Chart of Anodizing Steps

**Figure 2. Effects of Electrolyte Temperature on the
Optical Properties and Maximum Coating
Thickness of Oxalic Acid Anodizing (at
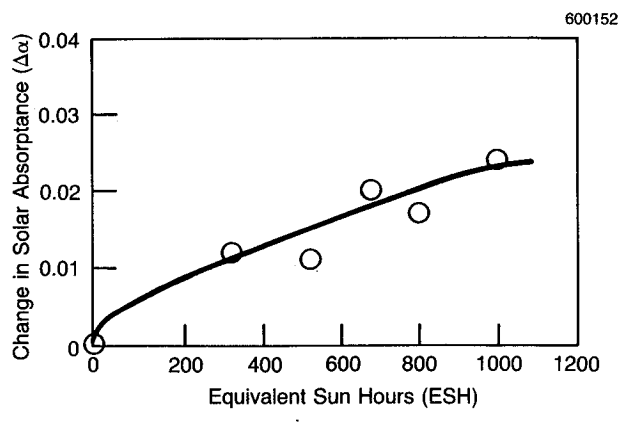15% Oxalic Acid and 10 A/sq ft)**

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Figure 3. Change in Solar Absorptance vs Equivalent
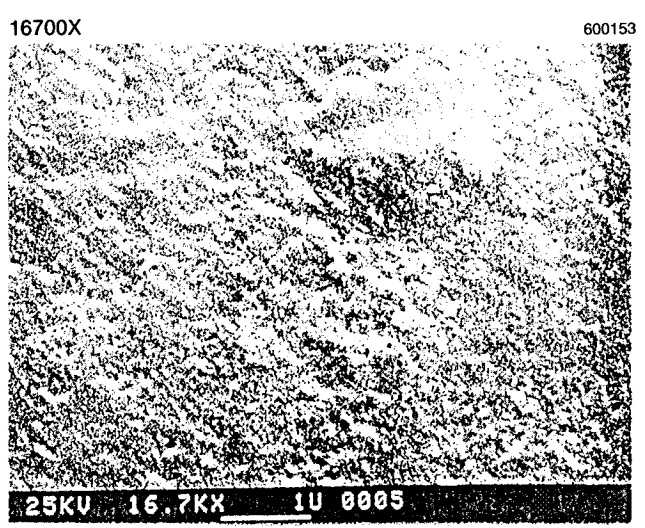Sun Hours Exposed for Oxalic Acid Anodized
Sample

Figure 4. Surface Morphology of Oxalic Acid Anodized
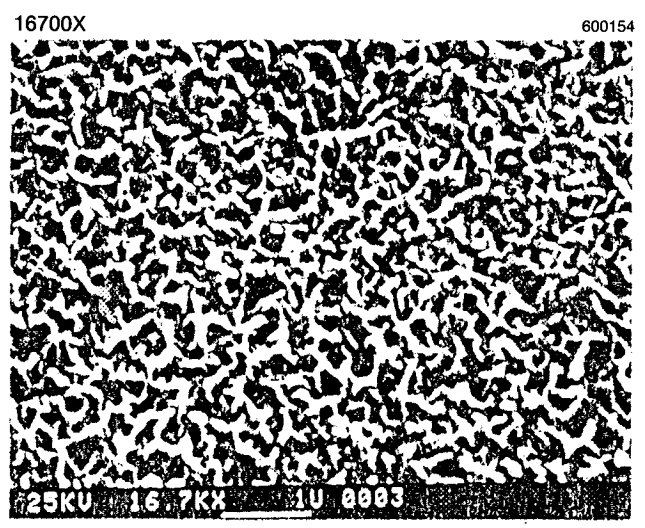Coating Produced at 30°C

Figure 5. Surface Morphology of Oxalic Acid Anodized
Coating Produced at 50°C

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