

## **Thin-Film Sulfuric Acid Anodizing as a Replacement for Chromic Acid Anodizing**

By

**K.J. Kallenborn**  
**Rocketdyne Division**  
**Rockwell International Corporation**  
**6633 Canoga Avenue**  
**Canoga Park, CA 91303**

**J.R. Emmons**  
**Rocketdyne Division**  
**Rockwell International Corporation**  
**6633 Canoga Avenue**  
**Canoga Park, CA 91303**

Chromic acid has long been used to produce a thin, corrosion resistant (Type I) coating on aluminum. Following anodizing, the hardware was sealed using a sodium dichromate solution. Sealing closes up pores inherent in the anodized coating, thus improving corrosion resistance. The thinness of the brittle coating is desirable from a fatigue standpoint, and chromium was absorbed by the coating during the sealing process, further improving corrosion resistance. Unfortunately, both chromic acid and sodium dichromate contain carcinogenic hexavalent chromium. Sulfuric acid is being considered as a replacement for chromic acid. Sulfuric acid of 10-20% concentration has traditionally been used to produce relatively thick (Types II and III) or abrasion resistant (Type III) coatings. A more dilute, that is five weight percent, sulfuric acid anodizing process, which produces a thinner coating than Type II or III, with nickel acetate as the sealant has been developed. The process was evaluated in regard to corrosion resistance, throwing power, fatigue life, and processing variable sensitivity, and shows promise as a replacement for the chromic acid process.

### **Introduction**

Aluminum hardware at Rocketdyne is chromic acid anodized primarily for corrosion resistance, which sealing further improves. Therefore, corrosion testing is a necessary step in evaluating replacements for chromic acid for anodizing and sodium dichromate for sealing. Chromic acid anodized coupons must pass a 336-hour salt fog test per ASTM B117, so thin-film sulfuric acid anodized coupons were subjected to the same test. Galvanic corrosion has been a problem in the past, so the relative performance of the anodized coatings under galvanic conditions was examined. Also, the atmospheric corrosion resistance of the two anodized coatings was evaluated using actual hardware.

Published literature has shown that fatigue life is dependent upon anodized coating thickness - the thicker the coating, the shorter the fatigue life and the lower the endurance limit (Reference 1). This is due to the brittleness of the aluminum oxide layer. The fatigue specimens anodized in this study at various thin-film sulfuric anodizing parameters showed a wide range of endurance limits, so the relationship between endurance limit and anodized coating thickness was investigated to determine a maximum allowable coating thickness.

The chromic acid anodizing process is very tolerant of variations in processing variables. The anodizing bath temperature can range from 90 to 105°F. Manufacturing practice is to keep the hardware in the chromic acid anodizing bath until the current drops down to zero indicating that the reaction has stopped. This practice suggests that the chromic acid anodized coating goes to completion, that is, the coating reaches a thickness where the reaction stops and the coating does not get too thick. Also, all alloys are anodized under the same parameters and it would be desirable if the same could be done with thin-film sulfuric anodizing. It was necessary to determine the sensitivity of thin-film sulfuric coating thickness to processing variables such as bath temperature, anodizing voltage, and anodizing time, and whether the process goes to completion to develop parameters and tolerances for thin-film sulfuric acid anodizing. Throwing power - the ability to anodize in blind holes and passageways - of thin-film sulfuric anodizing was also evaluated and compared to the throwing power of chromic acid.

## Procedure

### *Sulfuric Acid Anodizing*

Coupon specimens were tightly positioned in an aluminum anodizing rack and processed as follows in a laboratory-scale line:

- 1) Degrease - 20 vol. percent Turco 3878 LF-NC at 145-160°F for 10 minutes;
- 2) Rinse in deionized (D.I.) water spray;
- 3) Alkaline clean - 6-8 oz./gal. Turco 4090 at 150-190°F for 7 minutes;
- 4) Rinse in D.I. water spray;
- 5) Deoxidize - 16 oz./gal. Turco Smut-Go NC plus 4 oz./gal. HNO<sub>3</sub> at room temperature for 15 minutes with air agitation;
- 6) Rinse in D.I. water spray;
- 7) Anodize - 3-7 weight percent sulfuric acid at 66-72°F at 15-25 volts for 5-120 minutes with air agitation and lead cathodes on all four sides of the tank, voltage slowly ramped from 0 to voltage of interest;
- 8) Rinse in D.I. water spray;
- 9) Seal - 2% Novamax Anoseal 1000 nickel acetate solution at 160-190°F for 10 minutes (with mechanical stirring prior to adding specimens);
- 10) Rinse - D.I. water at 175-185°F for 10 minutes.

The panels for galvanic corrosion testing and the hardware for atmospheric corrosion were processed on a manufacturing line at Rockwell Space Systems Division at Downey, CA to parameters similar to those above.

### *Chromic Acid Anodizing*

Control specimens were chromic acid anodized on the Rocketdyne production line per Rocketdyne specification RA0109-021, Type I Chromic Acid Anodizing. The procedure consists of degreasing, alkaline cleaning, deoxidizing, anodizing, and sealing. The anodizing is done in 4-8% chromic acid at 90-105°F at 40±1 volts. The hardware is left to anodize until the voltage drops to zero. Sealing is done in 1.3-2.2 oz./gal. sodium dichromate at 195-205°F for 20 minutes.

### *Corrosion Testing*

Salt fog corrosion testing was done at Rockwell Space Systems Division. Five panels 10 in. x 3 in. x 0.050 in. were tested for each anodizing and sealing condition. The alloy 2024 was used, as it is inherently the least corrosion-resistant and produces the thinnest anodized coating of the alloys of interest. The panels were racked at an angle of 5% from vertical and exposed to a 5% salt fog for 336 hours (14 days). The panels were examined visually at up to 100 times magnification for corrosion and evaluated with respect to ASTM B117 which states, "...test specimens shall show no more than a total of 15 isolated spots or pits, none larger than 0.031 inch in diameter, in a total of 150 square inches of test area grouped from five or more test pieces; nor more than 5 isolated spots or pits none larger than 0.031 inch in diameter, in a total of 30 square inches from one or more test pieces: except those areas within 0.062 inch from identification marks, edges, and electrode contact marks remaining after processing." The sulfuric acid specimens were anodized using 5% sulfuric acid, 25 volts, at 70°F for 20 minutes. The sealing was done using sodium dichromate or Anoseal 1000. The chromic acid specimens were anodized per RA0109-021.

The galvanic corrosion specimens consisted of 4 in. x 4 in. x 0.030 in. anodized panels of 2024, 6061, 7075, and Tens-50 alloys. One panel of each alloy was anodized in sulfuric acid and one of each in chromic acid for a total of eight panels. Each panel had a hole 0.25 in. in diameter punched in the center. Through this hole was fitted a screw, a nut, and two washers, all of brass, to form a galvanic couple (Figure 1). The panels were exposed to a 5% salt fog environment like the salt fog corrosion specimens above except that the specimens were exposed for 168 hours.

The atmospheric exposure test specimens consisted of scrapped valve housings, which are Tens-50 castings. The housings are approximately 12 inches in diameter by 4 inches thick. One specimen was anodized in sulfuric acid and one in chromic acid. The hardware was initially exposed to a suburban environment for five months, and then to a coastal environment for nine months.

### *Fatigue Testing*

High cycle fatigue testing was performed at Metcut Research Associates, Inc., Cincinnati, Ohio under the following conditions:

Mode - cantilever load control;  
Stress ratio -  $R = 0.1$   
Frequency - 30 Hz  
Waveform - sinusoidal  
Atmosphere - air  
Temperature - room  
Machine - calibrated Sonntag SF-1-U rotating mass type universal fatigue

Stress levels for the different alloys were chosen such that failures would be evenly distributed between  $10^4$  and  $10^7$  cycles. Flexural fatigue specimens were machined from 0.08 inch thick sheet of each alloy, 2024-T3, 6061-T4, and 7075-T6.

### *Throwing Power*

A test specimen for evaluating throwing power consisted of a flat 3 in. x 3 in. x 0.030 in. 2024 aluminum panel with a nylon block screwed tightly to it, Figure 2. The nylon block has a groove machined into it so that when it is attached to the aluminum panel, it simulates a blind hole in a piece of hardware. The specimens were specifically designed to be easy to fabricate and analyze. The block can be removed following anodizing and reused with other panels. The 2024 alloy was chosen for this study because, of the three wrought alloys evaluated, it is the hardest to anodize since it consistently produces the thinnest coating. Panels were anodized in 5% sulfuric acid at 70°F and 20 volts for times of 5 to 60 minutes. A panel was also anodized in chromic acid per RA0109-021.

## **Results and Discussion**

### *Corrosion Testing*

Table 1 shows the results of salt fog corrosion testing. Alloy 2024 was used for this test because it has the least corrosion resistance and produces the thinnest coating at any given anodizing condition of the alloys being evaluated. This test compared the effectiveness of thin-film sulfuric acid anodizing and the effectiveness of nickel acetate sealing. The chromic acid specimens showed no pitting and were oxide-free over the entire surface of the panels. The thin-film sulfuric specimens sealed with sodium dichromate showed one pit for the set with the remainder of the panels being oxide-free. The thin-film sulfuric specimens sealed with nickel acetate showed one pit for the set with some edge corrosion, but edge corrosion is exempted by ASTM B117. Although the sulfuric acid specimens showed a pit and the nickel acetate specimens showed some edge corrosion, these specimens passed ASTM B117 making them acceptable processes.

All galvanic corrosion specimens showed severe corrosion after 168 hours in salt fog. It was not expected that anodizing would provide much protection against galvanic corrosion. Based on visual examination of the panels, and cross-sections of the corroded area, it was concluded that the chromic acid anodized panels and the sulfuric acid anodized specimens performed similarly.

After five months in a suburban environment, the sulfuric acid anodized hardware and the chromic acid anodized hardware showed no degradation. The hardware had experienced a little rain and fog. After

nine months in a coastal environment, the anodized portions of the hardware showed no degradation while the areas of the hardware that were not anodized showed the beginnings of corrosion.

Table 1. Results of salt fog testing per ASTM B117 on anodized 2024 aluminum

Anodizing Process	Sealant	# Pits/Set	Pass/Fail	Coating Thickness, mils	Comments
Chromic	Sodium Dichromate	0	Pass	0.09	Oxide-Free Panels
Thin-Film Sulfuric	Sodium Dichromate	1	Pass	0.14	Oxide-Free Panels
Thin-Film Sulfuric	Anoseal 1000	1	Pass	0.12	Some Edge Corrosion

#### *Fatigue Testing*

Figures 3 through 5 show the plots of anodized coating thickness versus endurance limit for the alloys 2024, 6061, and 7075. Clearly, there is a relationship between coating thickness and fatigue life for thin-film sulfuric acid anodized specimens and it is possible to achieve an endurance limit equal to or greater than that of chromic acid anodized aluminum given a thin enough coating. By comparing the endurance limit of the chromic acid anodized specimens with the sulfuric acid anodized specimens, it can be seen that for all three alloys, the endurance limit begins to fall below that of the chromic acid anodized specimens at a coating thickness greater than 0.2 mils. This agrees with published observations (Reference 1) where it was found that anodized coating thicknesses between 0.2 and 0.3 mils began to affect fatigue life.

#### *Throwing Power*

Figure 6 shows the results of the throwing power tests. The sulfuric acid specimens showed a decrease in coating thickness with increasing depth into the blind hole. The coating thickness at the base of the hole varied from 24 to 44% of the coating thickness at the outside surface of the hole. In general, the ratio of coating thickness at the base of the hole to the coating thickness on the outside surface decreases with increasing anodizing time. This shows that even by increasing the anodizing time, the thickness inside the hole never catches up to the outside thickness; suggesting that the process is not going to completion. As a comparison, a specimen was anodized in chromic acid and it too showed a decrease in coating thickness with increasing depth into the blind hole. These results show that the throwing power of 5% sulfuric acid is no worse than the throwing power of chromic acid.

#### *Process Tolerance*

The effect of various processing variables on coating thickness is shown in Figures 7 through 9. Figure 7 shows the effect of changes in temperature with voltage and time held constant. The thin-film sulfuric acid process is fairly temperature sensitive, and to the same degree for all three alloys. If all alloys are to be anodized under the same conditions, the temperature of the bath should be kept at 72°F or less when using 20 volts for 20 minutes to keep the coating thickness at 0.2 mil or less for fatigue life. The process is also sensitive to voltage, especially the 6061 and 7075 alloys, Figure 8. If all alloys are to be anodized under the same conditions, at 70°F for 20 minutes, the voltage should be kept at 20 volts or less to keep the thickness at 0.2 mil or less. The results of the time versus thickness tests, Figure 9, show a strong dependence of thickness on time. Optimum anodizing conditions for a 5% sulfuric solution would be 70°F and 20 volts for 20 minutes. The tolerance on these variables is tight:  $\pm 1$  volt;  $\pm 2^\circ\text{F}$ ; and  $\pm 2$  minutes.

Coating thicknesses of the 6061 alloy increased linearly to 0.96 mil in 120 minutes (Figure 9), strongly suggesting that the process does not go to completion with this alloy. Coating thicknesses of the 2024 alloy increased parabolically to 0.41 mil in 120 minutes. If the process does go to completion with this alloy, it would be at a point where the coating thickness is much greater than the recommended 0.2 mil. During anodizing of the coupons, the current slowly increased with time, also indicating that the process is not going to completion. In chromic acid anodizing, the current drops to zero, indicating that the process is complete. If the thin-film sulfuric acid anodizing process is to be successfully implemented, close control of the anodizing time, temperature, and voltage must be maintained, especially if all alloys are anodized with the same parameters.

## Conclusions

1. Thin-film sulfuric acid anodizing with nickel acetate sealing provides adequate corrosion resistance per ASTM B117.
2. Thin-film sulfuric acid anodized 2024, 6061, and 7075 alloys can have the same or greater fatigue life as chromic acid anodized specimens provided the coating thickness is 0.2 mil or less.
3. The throwing power of 5% sulfuric acid is comparable to the throwing power of chromic acid.
4. The 5% sulfuric acid anodizing process does not go to completion.
5. Close control of anodizing time, voltage, and temperature is very important to prevent overly thick coatings, especially if all alloys are to be anodized with the same parameters.

## Reference

1. Stickley, G.W., "Additional Studies of Effects of Anodic Coatings on the Fatigue Strength of Aluminum Alloys", *Proceedings, American Society for Testing Materials*, Vol. 60, 1960, pp. 577-588.

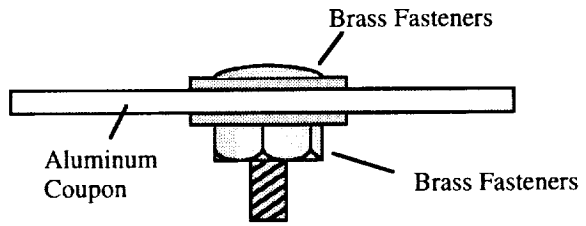


Figure 1. Cross-section of galvanic corrosion test specimen.

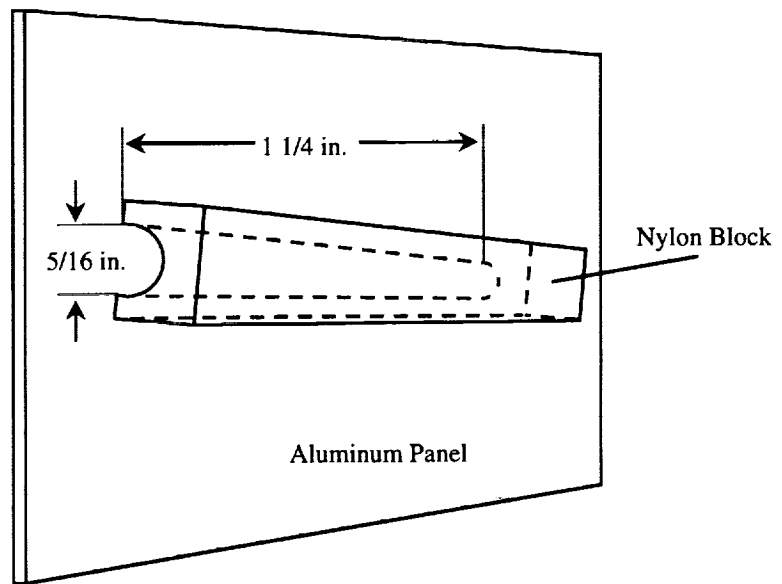


Figure 2. Throwing power test specimen.

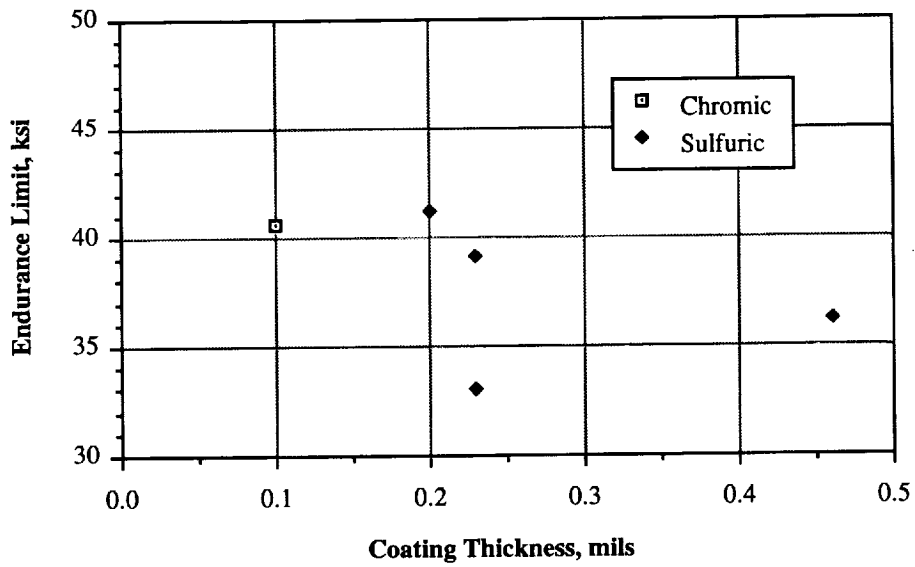


Figure 3. Endurance limit versus coating thickness of 2024 aluminum anodized in chromic and sulfuric acids.

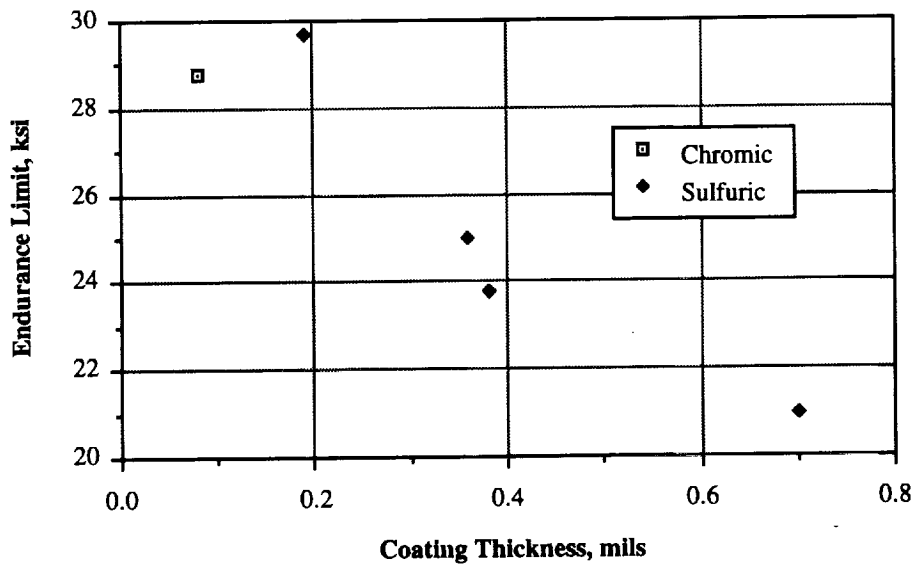


Figure 4. Endurance limit versus coating thickness of 6061 aluminum anodized in chromic and sulfuric acids.

C-4

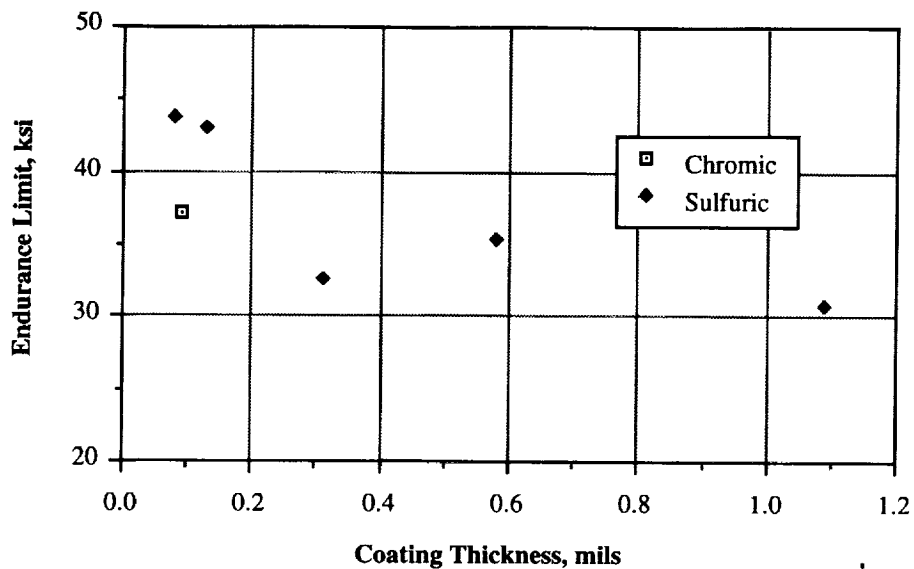


Figure 5. Endurance limit versus coating thickness of 7071 aluminum anodized in chromic and sulfuric acids.

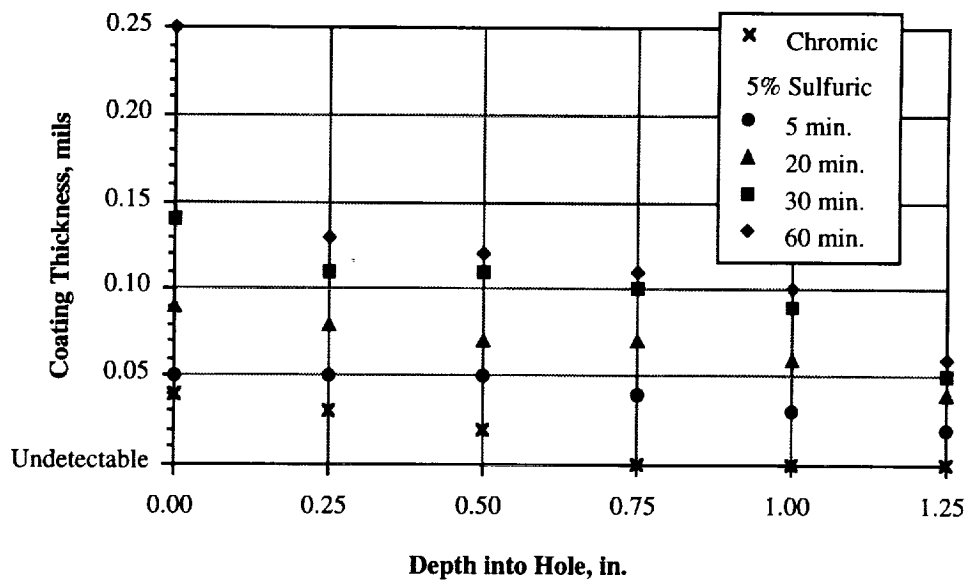


Figure 6. Anodized coating thicknesses versus depth into blind hole of throwing power test specimens of 2024 alloy. Sulfuric acid specimens were anodized at 70°F with 20 volts.



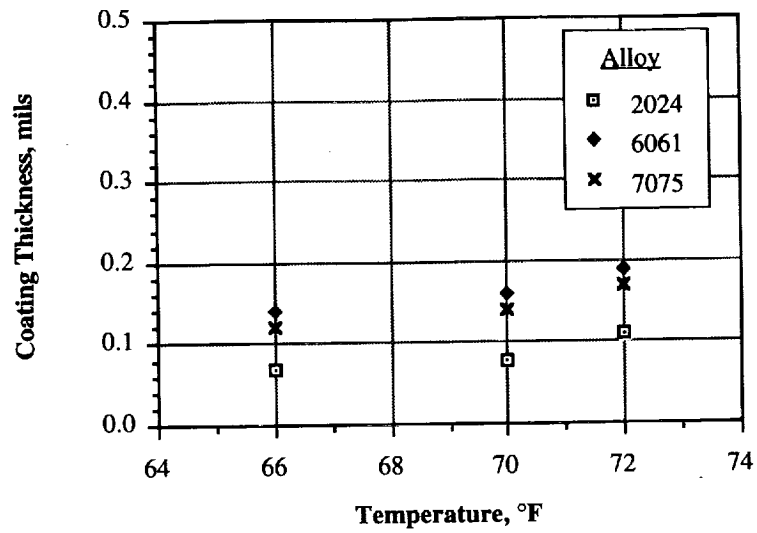


Figure 7. Effect of temperature on coating thicknesses of various alloys anodized in 5% sulfuric acid for 20 minutes at 20 volts.

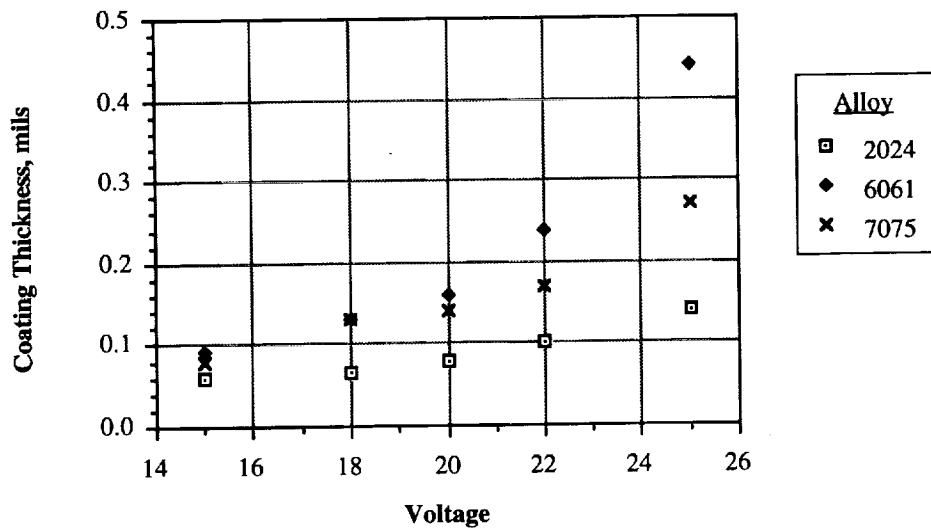


Figure 8. Effect of voltage on coating thicknesses of various alloys anodized in 5% sulfuric acid for 20 minutes at 70°F.

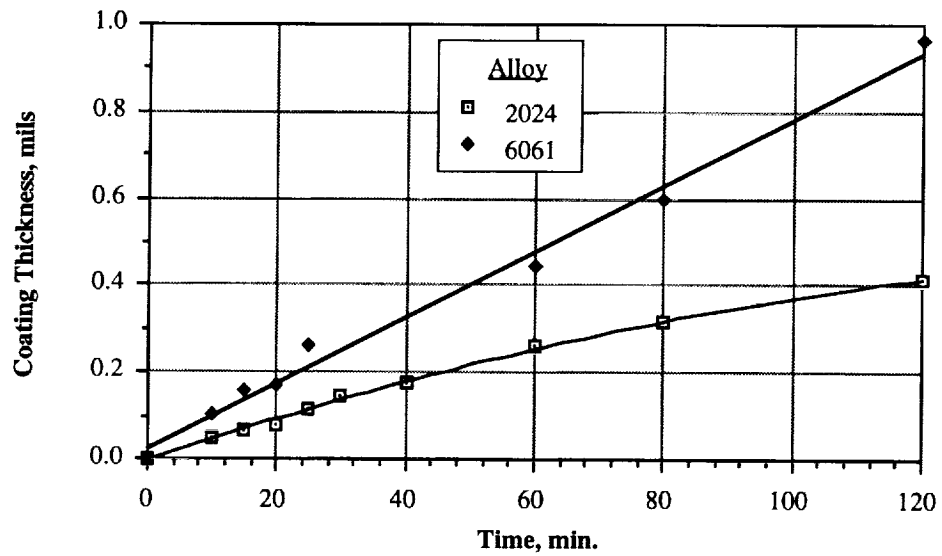


Figure 9. Effect of time on coating thicknesses of various alloys anodized in 5% sulfuric acid at 70°F and 20 volts.