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The Corrosion Protection of Several Aluminum Alloys by Chromic Acid and Sulfuric Acid Anodizing

M.D. Danford

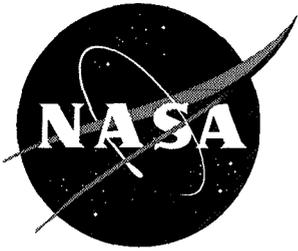
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TECHNICAL PAPER

THE CORROSION PROTECTION OF SEVERAL ALUMINUM ALLOYS BY CHROMIC ACID AND SULFURIC ACID ANODIZING

INTRODUCTION

Due to the severe restrictions being placed on the use of hexavalent chromium (a prime component of chromic acid anodizing) by federal and state mandates, it was deemed worthwhile to investigate the corrosion protection afforded aluminum (Al) alloys, by this method, and to compare them to the corrosion protection by sulfuric acid anodizing. Both electrochemical impedance spectroscopy (EIS), an alternating current (ac) method, and the direct current (dc) polarization resistance (PR) method were employed in this investigation.

Because results of the comparisons for Al alloys might be different for alloys of different compositions or tempers, several Al alloys differing in these respects were studied. In particular, 7075-T6 and 7075-T73 Al, 6061-T6 Al, and 2024-T3 Al were studied—each with both chromic acid and sulfuric acid anodizing. Results of these studies are presented in this report.

EXPERIMENTAL PROCEDURE

Flat plates, 10.2 by 15.2 cm (4 by 6 in), of 7075-T6 Al, 7075-T73 Al, 6061-T6 Al, and 2024-T3 Al were anodized using either the chromic acid (type I) or the sulfuric acid (type II) techniques. The anodized coat was removed on one side by either sanding or grit blasting to provide electrical contact. In general, plates anodized by the chromic acid technique provided a rather soft anodized coat which was easily removed by sanding. On the other hand, plates which were anodized using the sulfuric acid technique provided a rather hard, durable coat which had to be grit blasted for removal. The anodized plates were clamped into flat corrosion cells manufactured by EG&G-PARC and exposed to 3.5 percent sodium chloride (Na-Cl) at pH 5.4, a very corrosive medium. Corrosion data were obtained over a period of 27 days. Silver/silver chloride reference electrodes were used in all cases.

Both EIS (an ac method) and the PR technique (a dc method) were employed in this investigation. Generally, all plates were amenable to study by both methods, since corrosion currents were large enough to measure with the PR technique.

The EG&G-PARC model 378 ac impedance system was used for all corrosion measurements. For the EIS measurements, data were taken in three sections. The first two sections, beginning at 0.001 and 0.1 Hz, respectively, were obtained using the fast Fourier transform technique. The third data section, ranging from 6.28 to 40,000 Hz, was collected using the lock-in amplifier technique. The sequencing was performed automatically using the autoexecute procedure, with all data merged to a single set for each run. After collection, these data were processed and analyzed by computer using the models of figures 1 and 2. The same computer also controlled the experiment.

Data for the PR technique were collected using the same instrumentation with the EG&G-PARC model 342C software, which was developed especially for dc measurements. Instrumentation developed

by EG&G-PARC automatically corrected the data for IR drop during the scan. The potential applied to the specimen during the scan varied from -20 to +20 mV on either side of the corrosion potential E_{CORR} , with data points (current and potential) being recorded in $1/4$ mV increments.

The primary equivalent circuit model for interpretation of EIS data is shown in figure 1. The circuit model of figure 2 was used to calculate the effect of diffusion polarization. The Warburg coefficient sigma is obtained using this model. The higher the value of sigma, the less the diffusion of the surrounding medium through the specimen coat. If the value of sigma exceeds that of the charge transfer parameter $R(T)$, the corrosion mechanism is diffusion controlled. Generally, there is a strong correlation between the pore resistance ($R(P)$)-time curves and sigma-time curves; that is, as the pore resistance becomes less, the diffusion through the coating increases. The development and selection of the models of figures 1 and 2 have been discussed previously.¹

Values of each of the circuit components in either figure 1 or 2 were treated as parameters in the nonlinear ORGLS² least squares programs, which automatically adjusted these parameters to obtain a best fit to the observed Bode magnitude data (log impedance versus $\log \omega$, where $\omega = 2\pi \times$ frequency). Good estimates of the corrosion rates were obtained from EIS data using the Stern-Geary equation for charge transfer control.³⁻⁵ Tafel constants (b_a and b_c) were assumed to be 50 mV each. The value of 50 mV for each of the Tafel constants has been found to provide excellent agreement with values of I_{CORR} obtained by the dc PR measurements.⁶ Corrosion rates are directly related to values of I_{CORR} and are determined from the I_{CORR} values by methods described previously.⁶

In the PR method, curves of potential versus current were obtained, and the data were analyzed using the program POLCURR.⁷ The theory for the PR technique has been described previously.⁸

RESULTS AND DISCUSSION

In this section, results are presented for 7075-T6, 7075-T73, 6061-T6, and 2024-T3 aluminum alloys. Pertinent results are summarized in table 1. Results for 2219-T87 aluminum alloy⁹ are included in table 1 for comparison purposes.

7075-T6 Aluminum

For the chromic acid anodizing case, the charge transfer resistance $R(T)$ -time curve is shown in figure 3, and the pore resistance $R(P)$ -time curve is shown in figure 4. Both curves show a general decrease in these parameters, indicating a general increase in corrosion rate of the Al metal and porosity of the coating. The sigma-time curve in figure 5 indicates an increase in diffusion with time, and the I_{CORR} -time curve in figure 6 shows that the corrosion rate is indeed increasing.

For the sulfuric acid case, the $R(T)$ -time curve is shown in figure 7, and the $R(P)$ -time curve in figure 8. The $R(P)$ -time curve actually indicates a slight rise in pore resistance with time. The sigma (σ)-time and I_{CORR} -time curves are shown in figures 9 and 10, respectively.

The corrosion rate for bare 7075-T6 Al is 7.02 mpy, the highest corrosion rate observed for any of the Al alloys in this study. Significant results are summarized in table 1. The percent reduction of the 27-day average from that of the base metal was 77.6 and 99.9 percent, respectively, for chromic acid and

sulfuric acid anodizing. The mean daily increase of I_{CORR} for the chromic acid case is 0.1605 $\mu\text{A}/\text{day}$, the highest value observed in this work.

7075-T73 Aluminum

$R(T)$, $R(P)$, and I_{CORR} -time curves for the 7075-T73 Al alloy anodized with the chromic acid technique are shown in figures 11 through 13. Because values of $R(T)$ and $R(P)$ had reached rather low values because of high corrosion currents, EIS measurements were stopped at 15 days and measurements were continued using only the PR method. Both $R(T)$ -time and $R(P)$ -time curves show steadily declining values. The I_{CORR} -time curve exhibits a large maximum at 13 days and drops to lower values thereafter.

The same curves for the sulfuric acid technique are shown in figures 14 through 16. The $R(T)$ -time curve oscillates rather extensively, but shows a slightly increasing value of this parameter with time. The $R(P)$ -time curve also shows a slightly increasing trend, while, as expected, the I_{CORR} -time curve slightly decreases with time.

The corrosion rate for bare 7075-T73 Al is 3.47 mpy, intermediate between those for 7075-Al and 2219-T87 Al. The percent reductions in corrosion currents were 90.6 and 99.99 percent for the chromic acid and sulfuric acid cases, respectively. The mean daily change in corrosion current (-1.69×10^{-6} mpy) for the sulfuric acid was the smallest observed in this work, as was the average value for the corrosion current.

6061-T6 Aluminum

For the chromic acid case, $R(T)$ -time, $R(P)$ -time, and I_{CORR} -time curves are shown in figures 17 through 19, respectively. The $R(T)$ -time curve, after an initial decrease, rises steadily until day 25, where it drops rapidly. The $R(P)$ -time curve decreases in value overall, while the I_{CORR} -time curve is oscillatory, but exhibits a slight overall increase in value.

$R(T)$ -time, $R(P)$ -time, and I_{CORR} -time curves for the sulfuric acid case are shown in figures 20 through 22, respectively. The $R(T)$ -time curve is generally decreasing, while the $R(P)$ -time curve shows a large maximum at 12 days, but steadily decreases thereafter. The trend in the I_{CORR} -time curve is generally toward higher values.

The corrosion rate for bare 6061-T6 Al was measured as 2.62 mpy, a little lower than that for 7075-T73 Al. As shown in table 1, the percent reductions of the 27-day average corrosion currents over that of the bare metal are 91.6 and 98.1 percent for the chromic acid and sulfuric acid cases, respectively.

2024-T3 Aluminum

For 2024-T3 Al, curves for the chromic acid case are shown in figures 23 through 25. Both the $R(T)$ -time and $R(P)$ -time curves, though oscillating, show a general overall decrease in value. The I_{CORR} -time curve in figure 25 shows a general increase in the value of the corrosion current with time.

Curves for the sulfuric acid case are shown in figures 26 through 28. The oscillating curves for $R(T)$ and $R(P)$ generally decrease in value. The I_{CORR} -time curve in figure 28 oscillates rather extensively, but, as table 1 shows, there is a positive mean daily increase in I_{CORR} .

The corrosion rate for the bare metal is 2.72 mpy, about the same as that for 6061-T6 Al. The percent reduction for the chromic acid case over that of the bare metal was only 76.4 percent, the lowest value observed in this work. The corresponding value for the sulfuric acid case was 93.3 percent. All other pertinent quantities are also shown in table 1.

CONCLUSIONS

For aluminum alloys 7075-T6, 7075-T73, 6061-T6, and 2024-T3, corrosion rate reductions are higher for sulfuric acid anodizing than for chromic acid anodizing in all cases. Also, in most cases, the mean daily increases of corrosion current are larger for chromic acid anodizing. Anodized coats produced by chromic acid anodizing are soft and easily removed. On the other hand, coats produced by sulfuric acid anodizing are harder and more durable. Furthermore, a thicker anodized coat is more easily achieved by sulfuric acid anodizing. Therefore, from this work, it is concluded that sulfuric acid anodizing is superior to chromic acid anodizing.

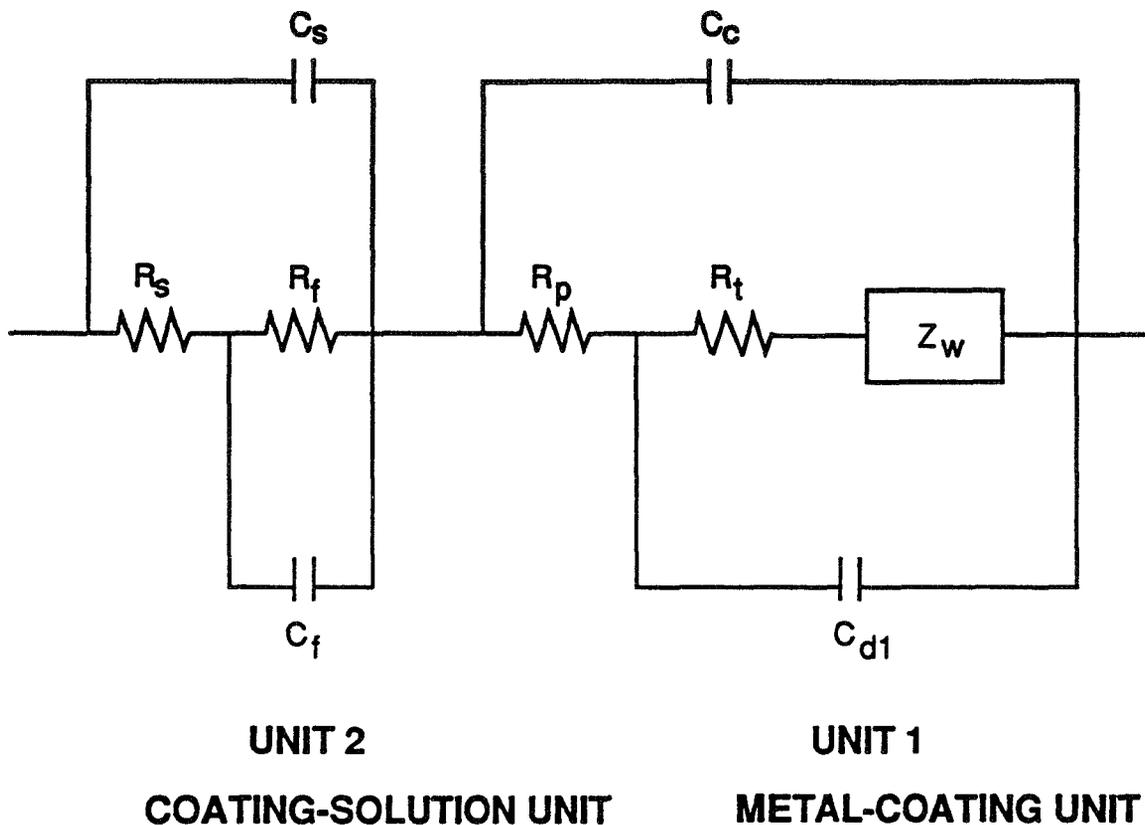
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9. Danford, M.D.: NASA Technical Memorandum TM-108383, November 1992.

Table 1. Average corrosion currents for anodized aluminum alloys with mean daily increase.

Material and Temper/ Anodize	7-Day (μA)	27-Day (μA)	Percent Increase	Mean Daily Increase	Percent Reduction Over Base Metal
<u>2219-T87*</u>					
Chromic Acid	0.0251	0.0654	160.2	0.00339	91.5
Sulfuric Acid	0.00957	0.01152	20.4	0.00016	98.5
<u>7075-T6</u>					
Chromic Acid	0.9600	2.6453	175.6	0.1605	77.6
Sulfuric Acid	0.01103	0.01822	65.2	0.0007	99.9
<u>7075-T73</u>					
Chromic Acid	0.0570	0.7047	1,142.3	0.0266	90.6
Sulfuric Acid	4.88×10^{-5}	5.87×10^{-5}	20.4	-1.69×10^{-6}	
<u>6061-T6</u>					
Chromic Acid	0.3581	0.4758	32.9	0.0074	91.6
Sulfuric Acid	0.0712	0.1094	53.7	0.0078	98.1
<u>2024-T3</u>					
Chromic Acid	0.6234	1.3930	123.4	0.0648	76.4
Sulfuric Acid	0.1075	0.3962	268.3	0.0186	93.3

*Included for comparison purposes.



- C_s SOLUTION CAPACITANCE
- R_s SOLUTION RESISTANCE
- C_f FARADAIC CAPACITANCE (COATING/SOLUTION)
- R_f FARADAIC RESISTANCE
- C_c COATING CAPACITANCE
- R_p COATING RESISTANCE
- R_t CHARGE TRANSFER RESISTANCE
- C_{d1} METAL/COATING INTERFACE CAPACITANCE
- Z_w WARBURG IMPEDANCE (DIFFUSION POLARIZATION)

Figure 2. Equivalent circuit model for calculating the Warburg coefficient.

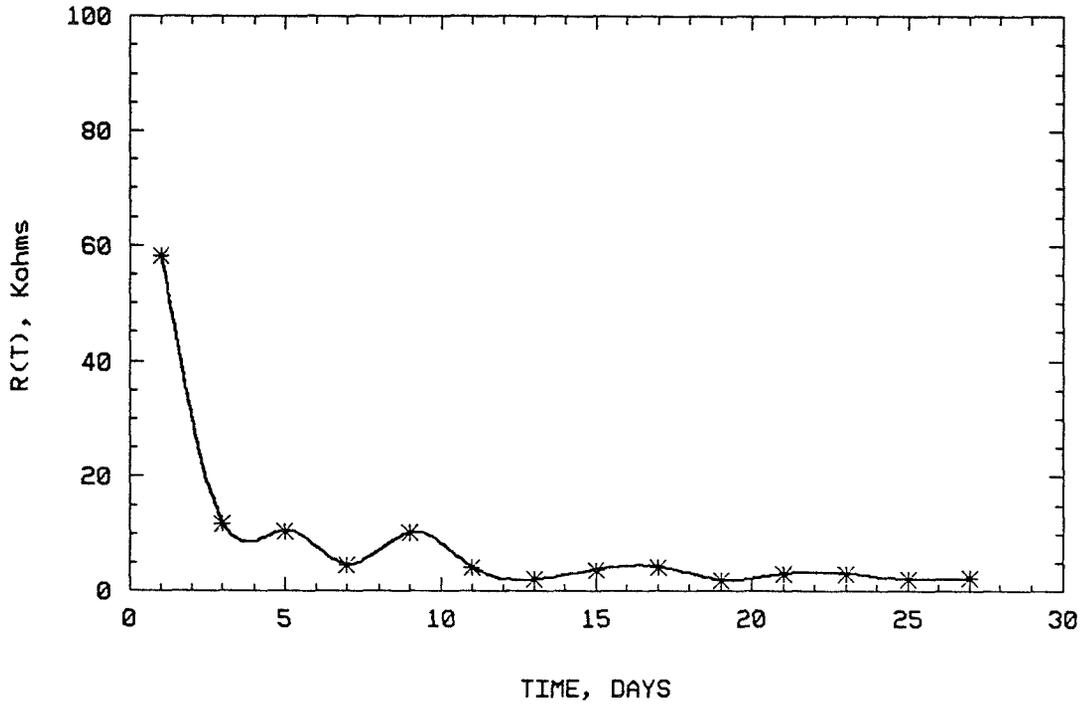


Figure 3. Charge transfer resistance, 7075-T6 Al, chromic acid anodize.

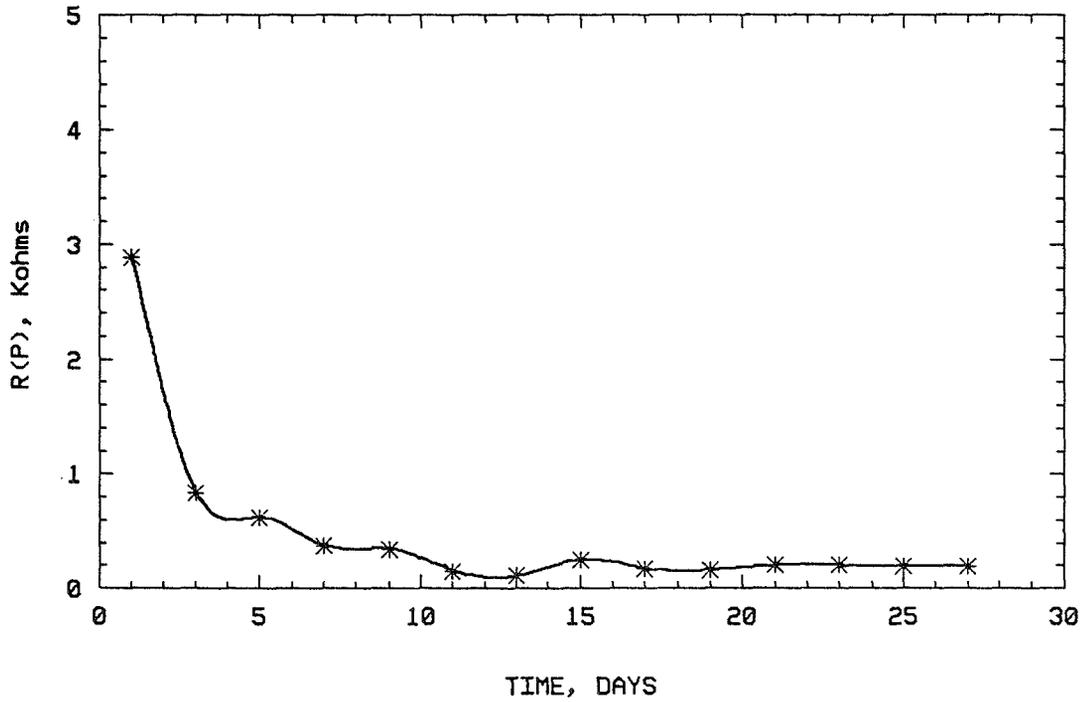


Figure 4. Pore resistance, 7075-T6 Al, chromic acid anodize.

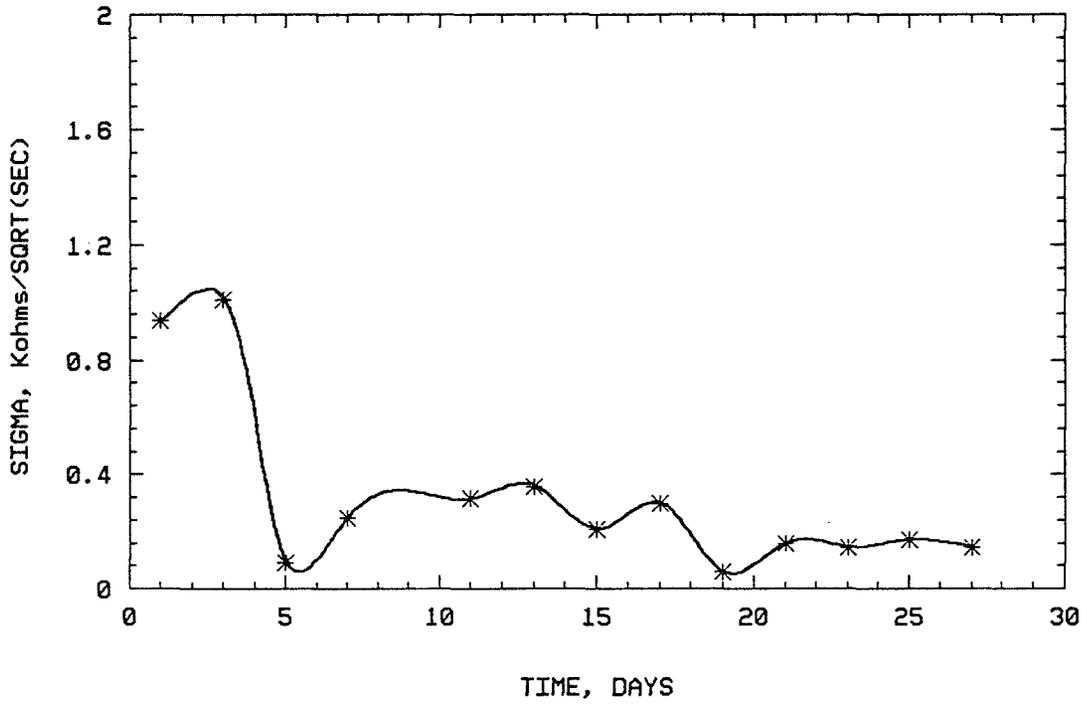


Figure 5. Warburg coefficient, 7075-T6 Al, chromic acid anodize.

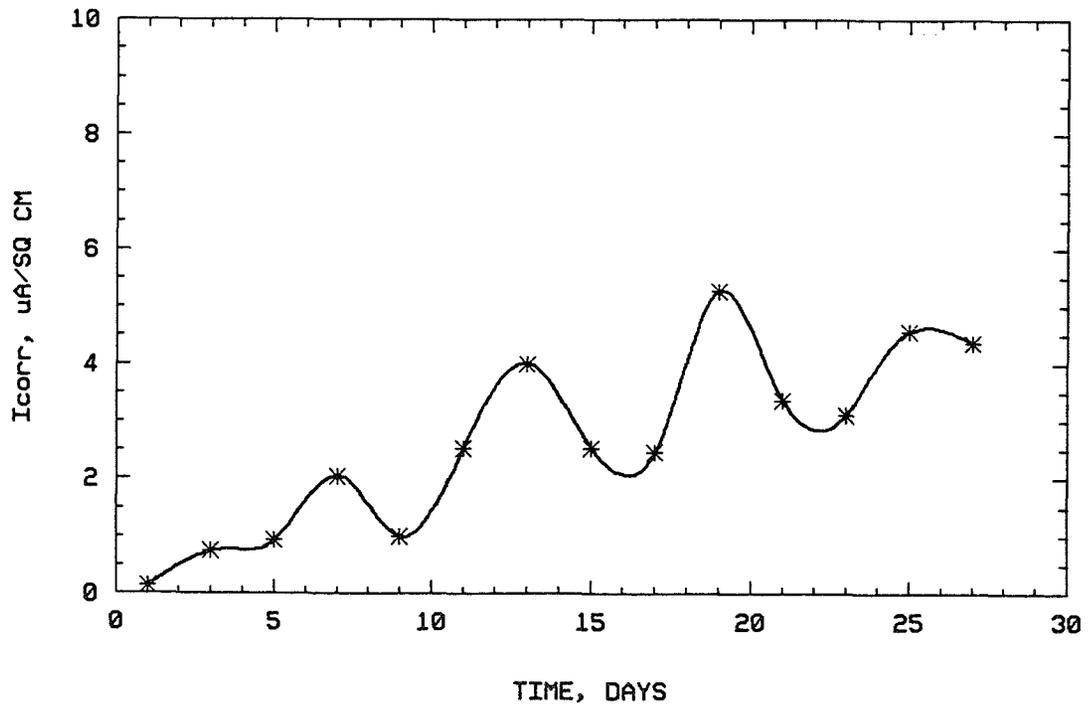


Figure 6. Corrosion current, 7075-T6 Al, chromic acid anodize.

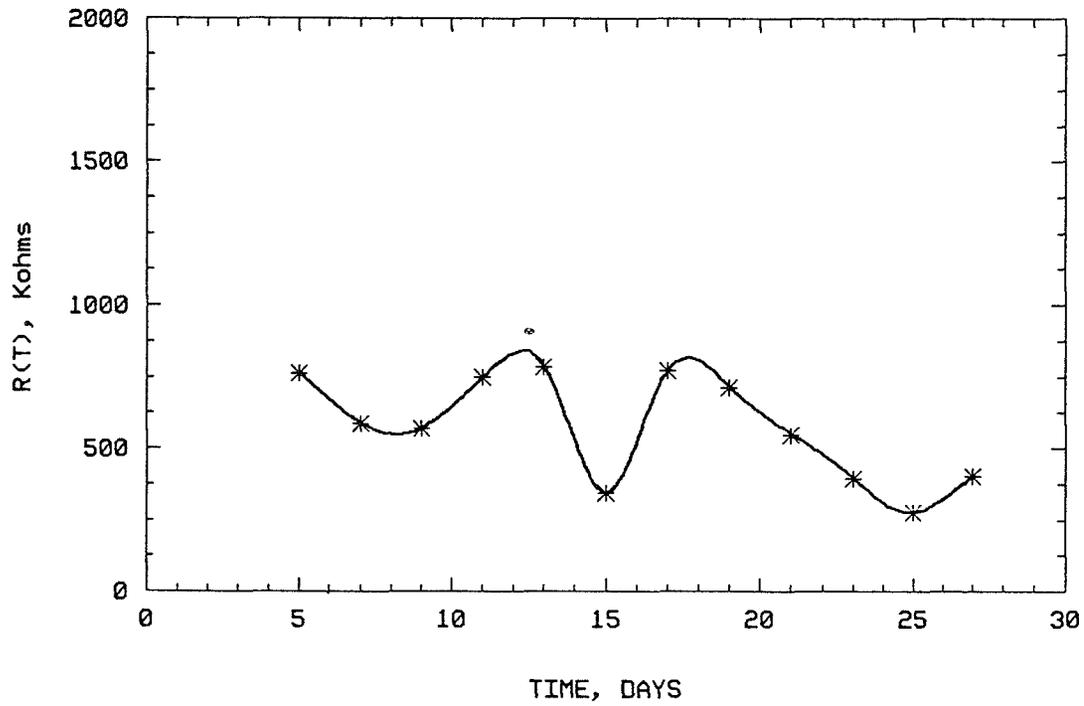


Figure 7. Charge transfer resistance, 7075-T6 Al, sulfuric acid anodize.

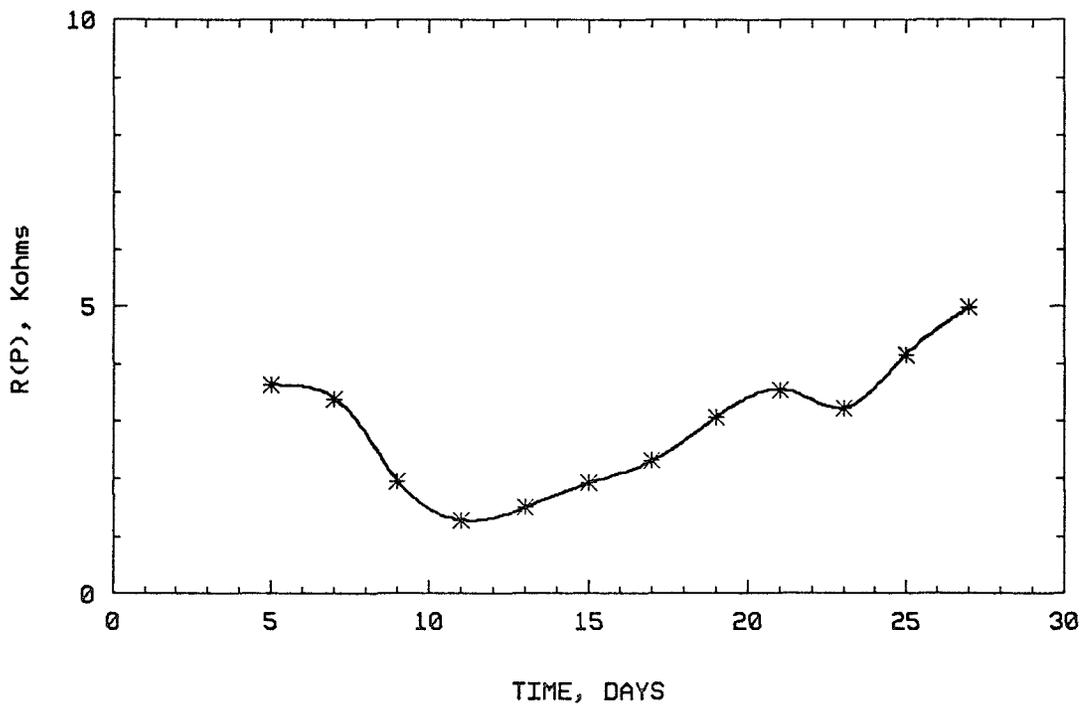


Figure 8. Pore resistance, 7075-T6 Al, sulfuric acid anodize.

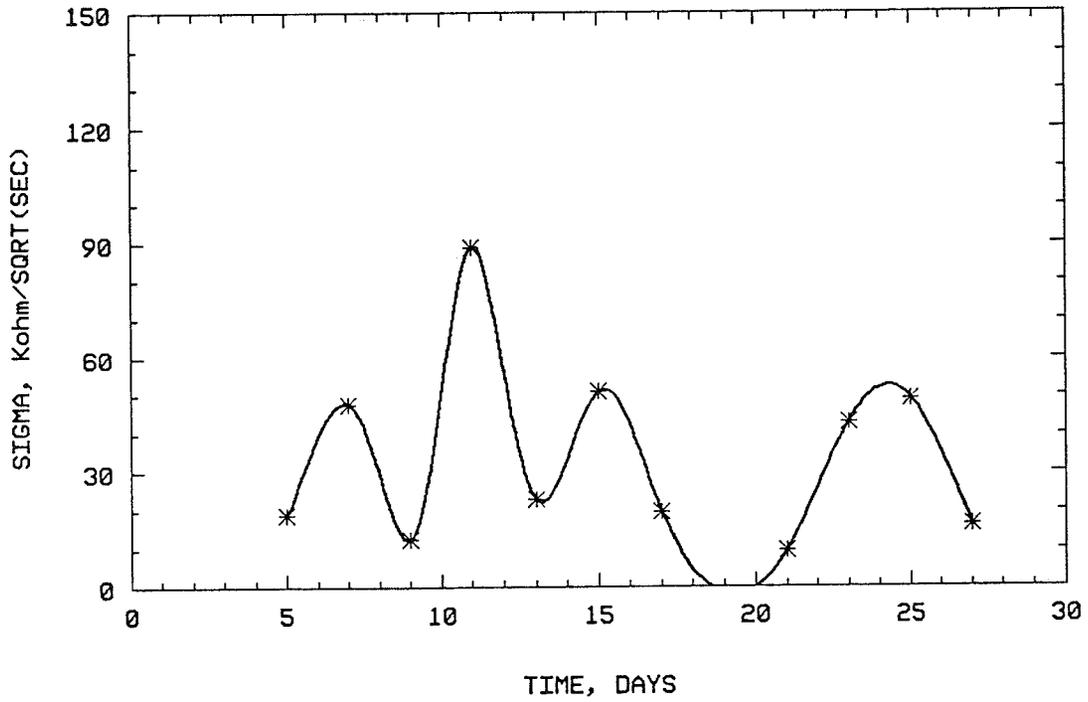


Figure 9. Warburg coefficient, 7075-T6 Al, sulfuric acid anodize.

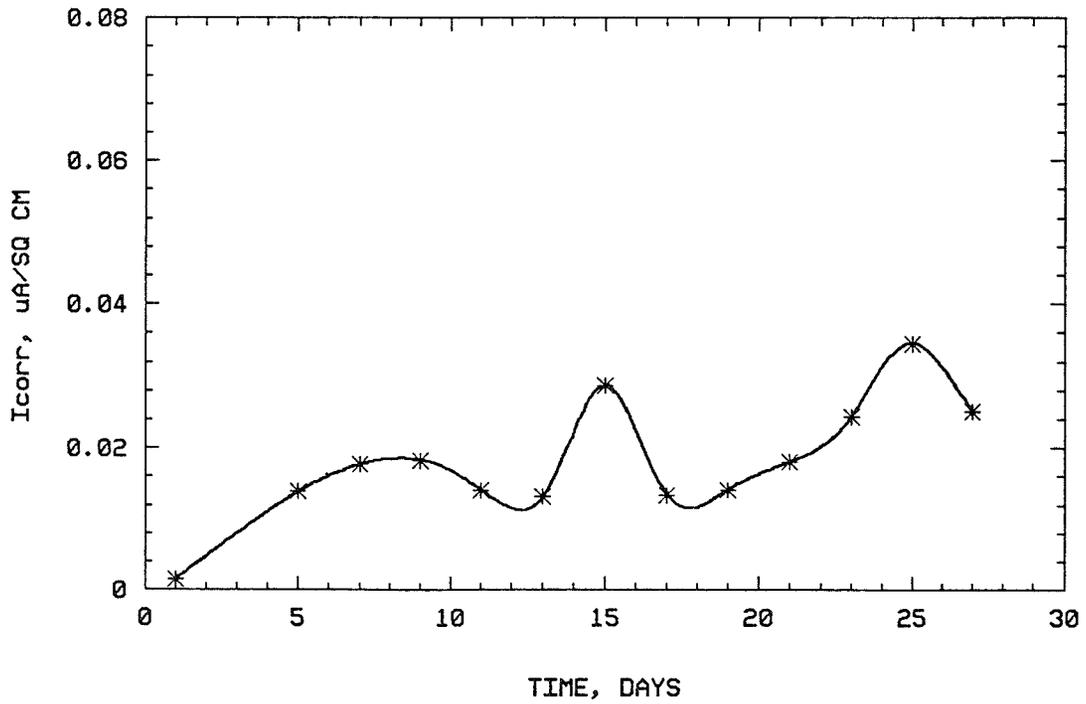


Figure 10. Corrosion current, 7075-T6 Al, sulfuric acid anodize.

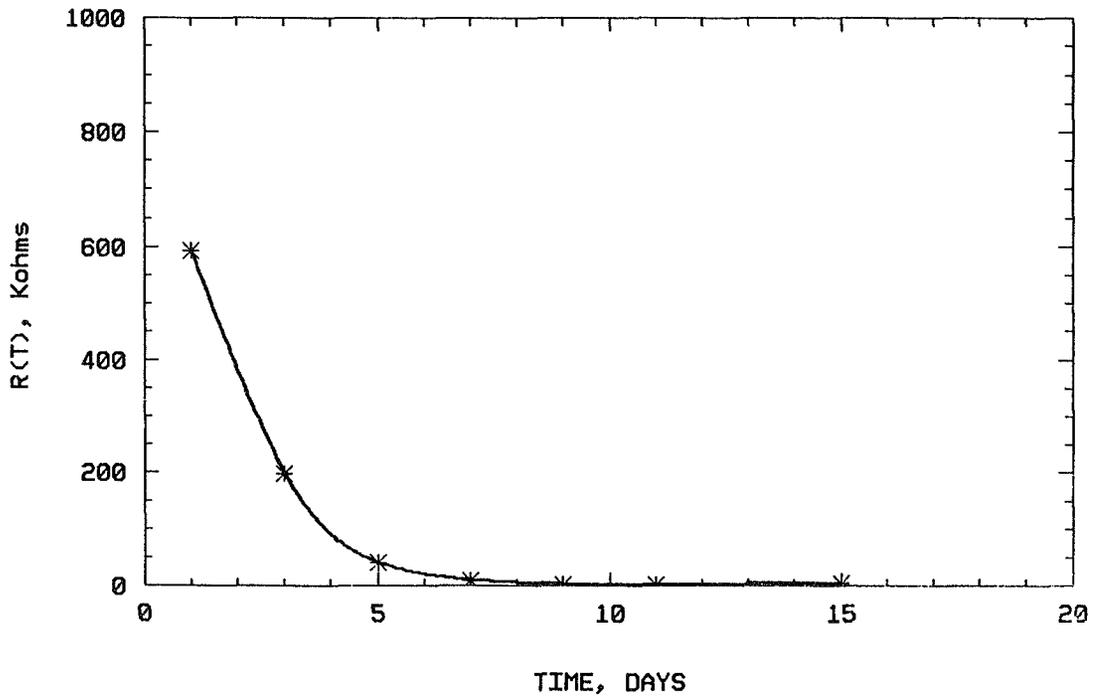


Figure 11. Charge transfer resistance, 7075-T73 Al, chromic acid anodize.

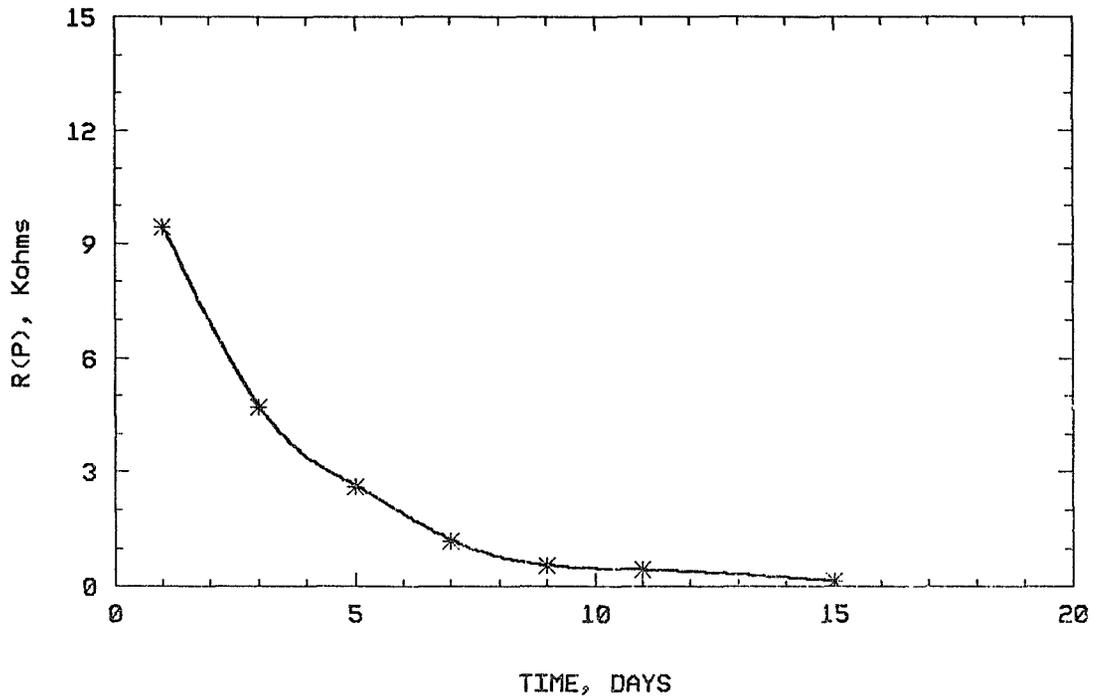


Figure 12. Pore resistance, 7075-T73 Al, chromic acid anodize.

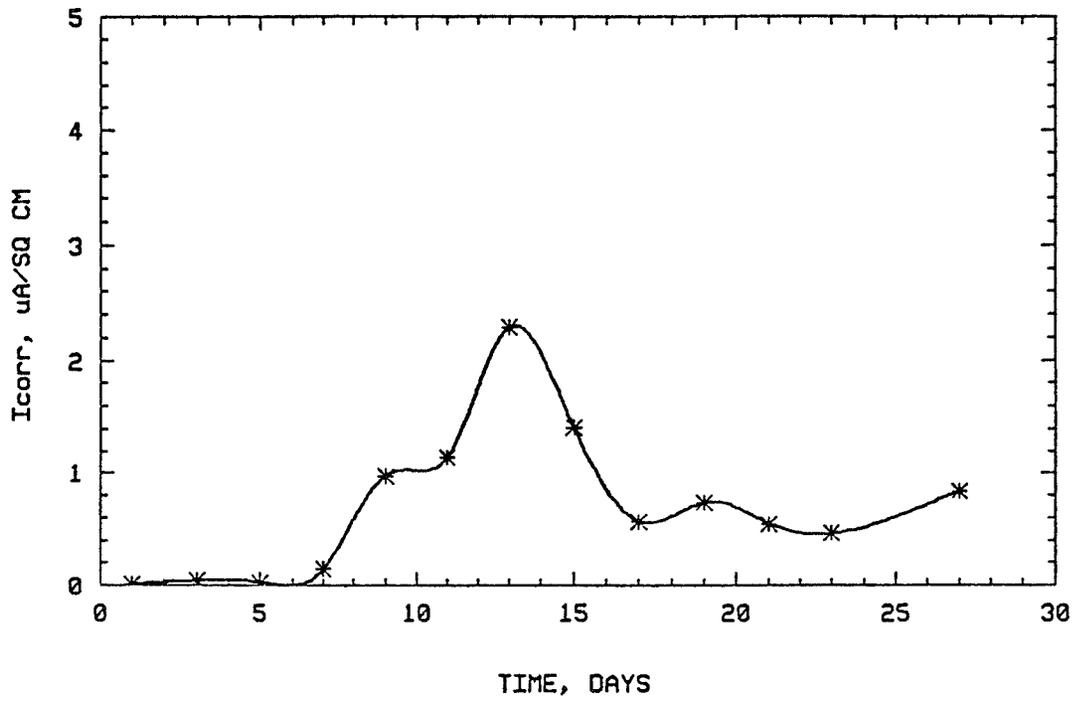


Figure 13. Corrosion current, 7075-T73 Al, chromic acid anodize.

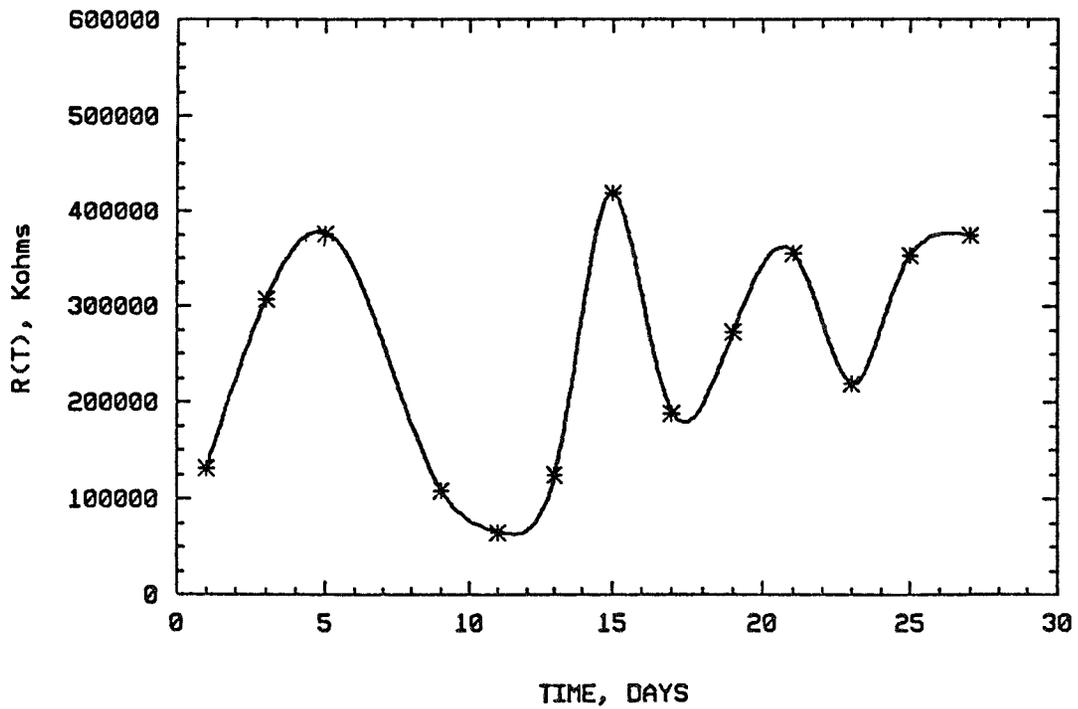


Figure 14. Charge transfer resistance, 7075-T73 Al, sulfuric acid anodize.

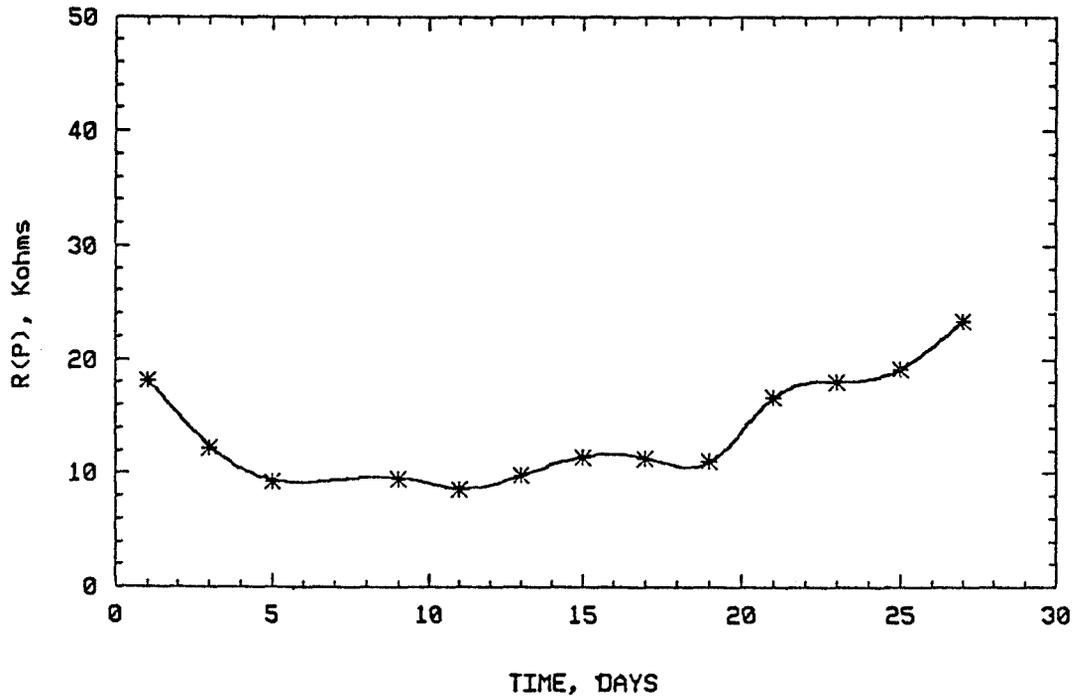


Figure 15. Pore resistance, 7075-T73 Al, sulfuric acid anodize.

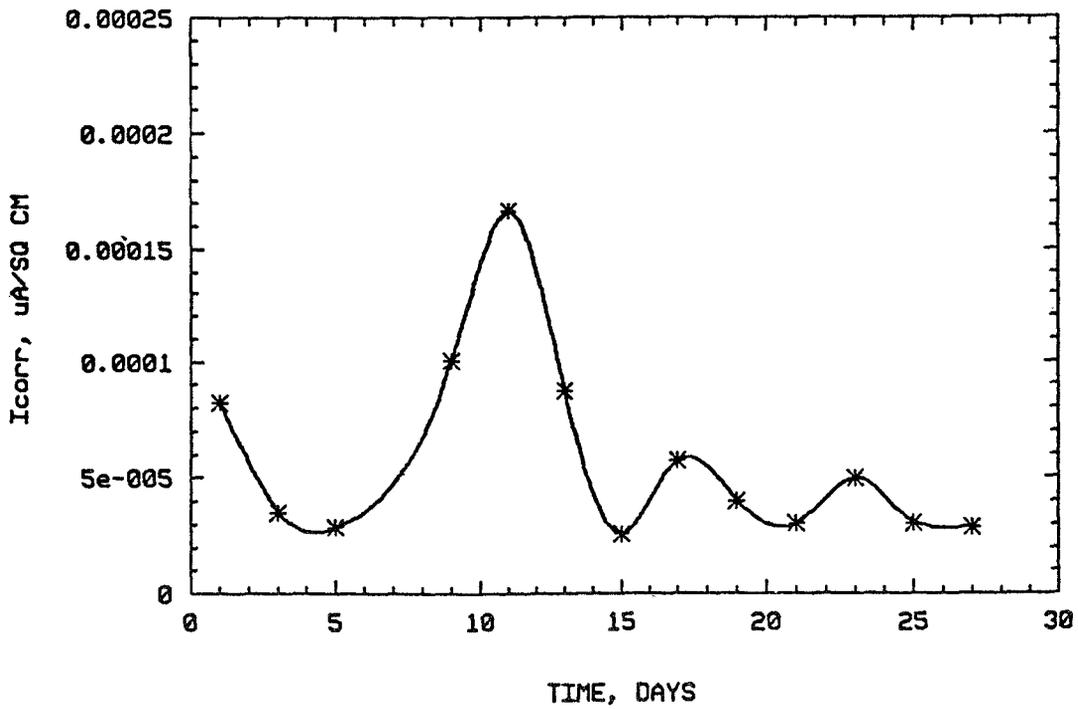


Figure 16. Corrosion current, 7075-T73 Al, sulfuric acid anodize.

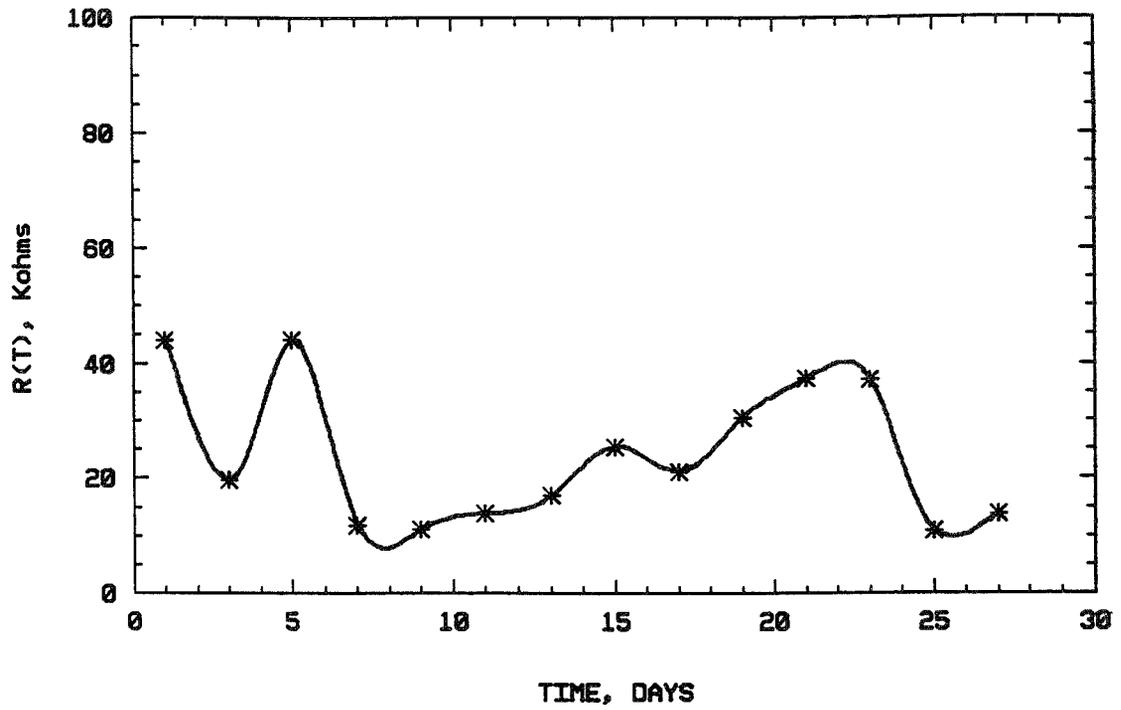


Figure 17. Charge transfer resistance, 6061-T6 Al, chromic acid anodize.

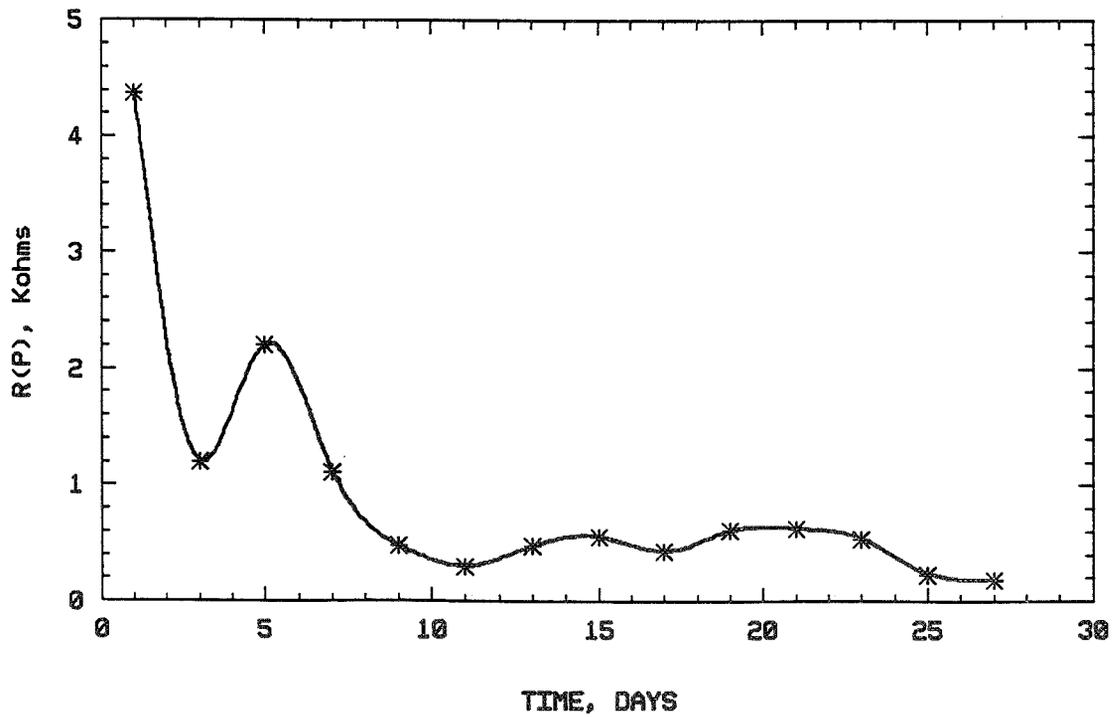


Figure 18. Pore resistance, 6061-T6 Al, chromic acid anodize.

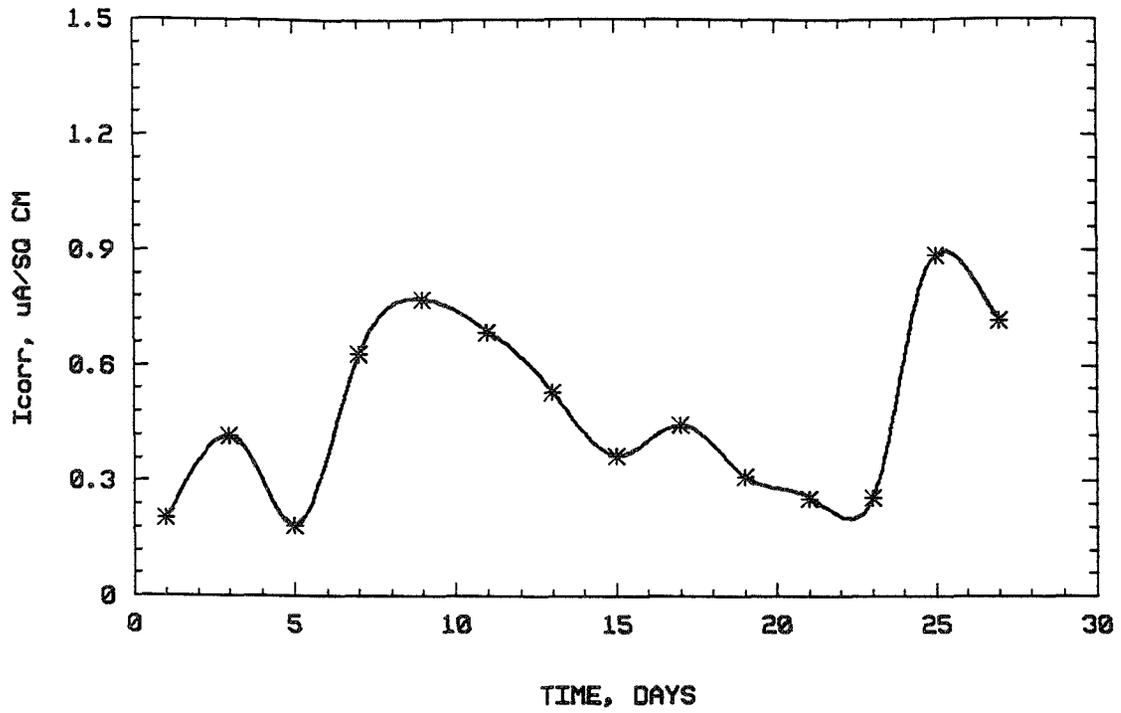


Figure 19. Corrosion current, 6061-T6 Al, chromic acid anodize.

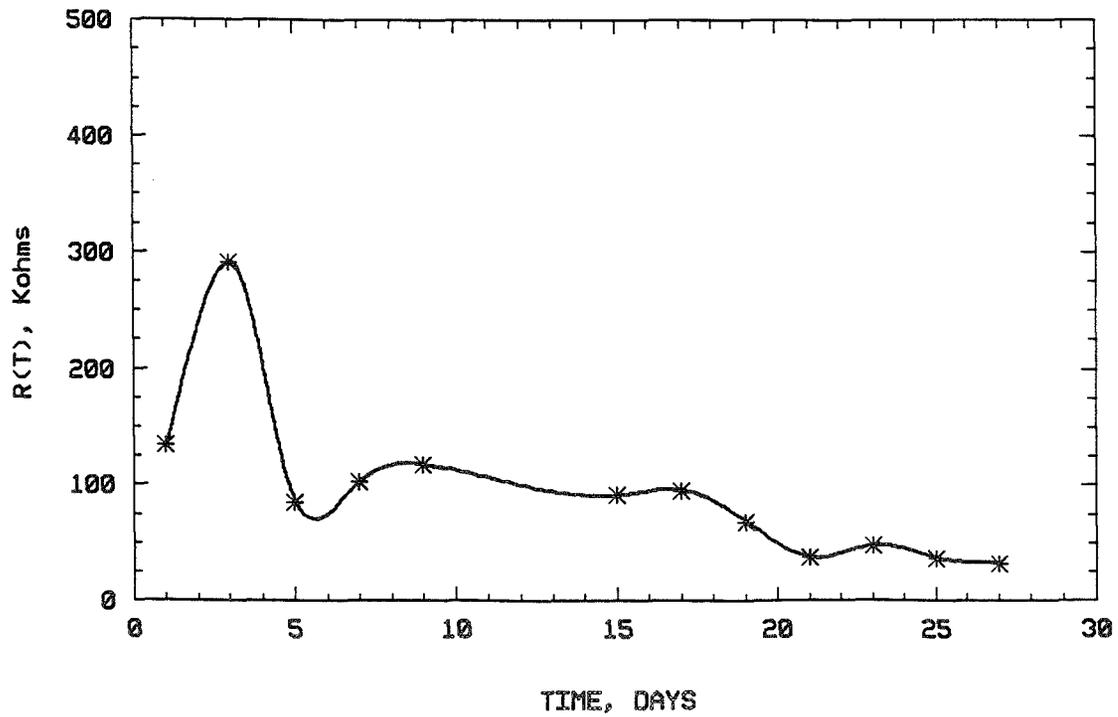


Figure 20. Charge transfer resistance, 6061-T6 Al, sulfuric acid anodize.

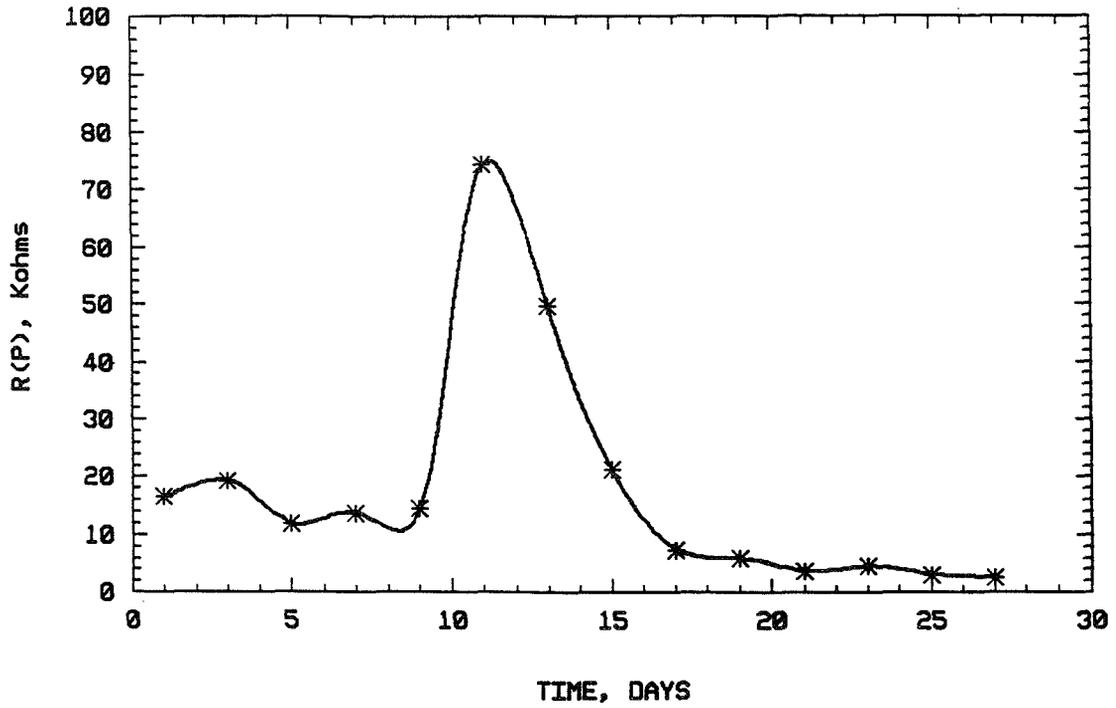


Figure 21. Pore resistance, 6061-T6 Al, sulfuric acid anodize.

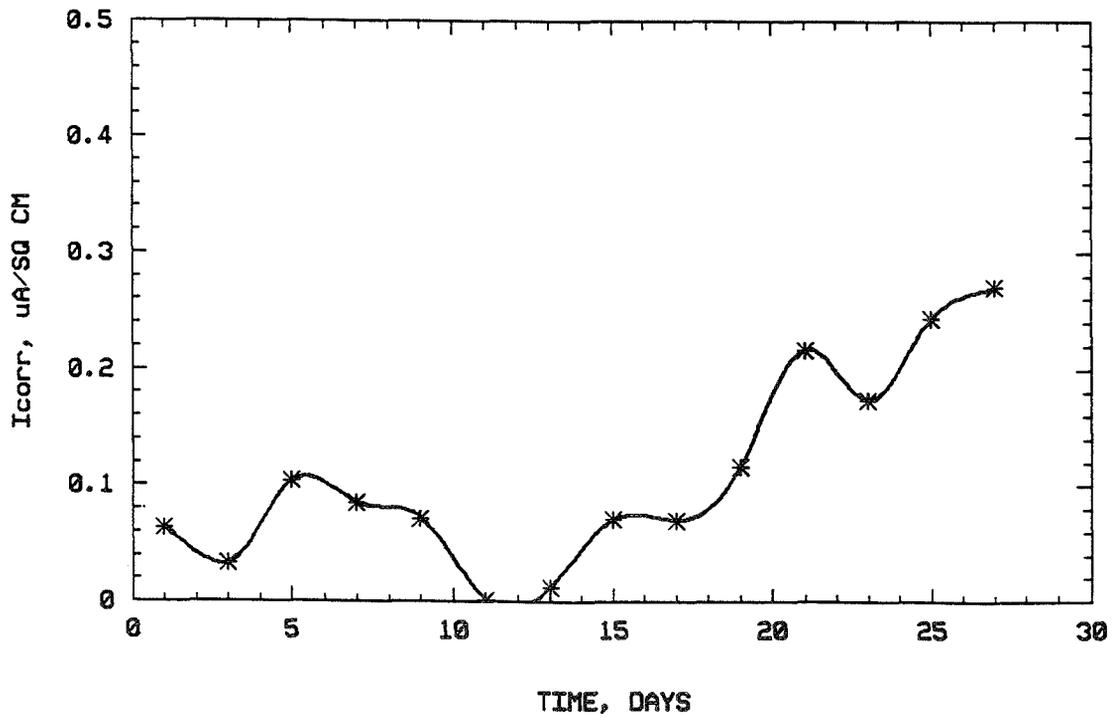


Figure 22. Corrosion current, 6061-T6 Al, sulfuric acid anodize.

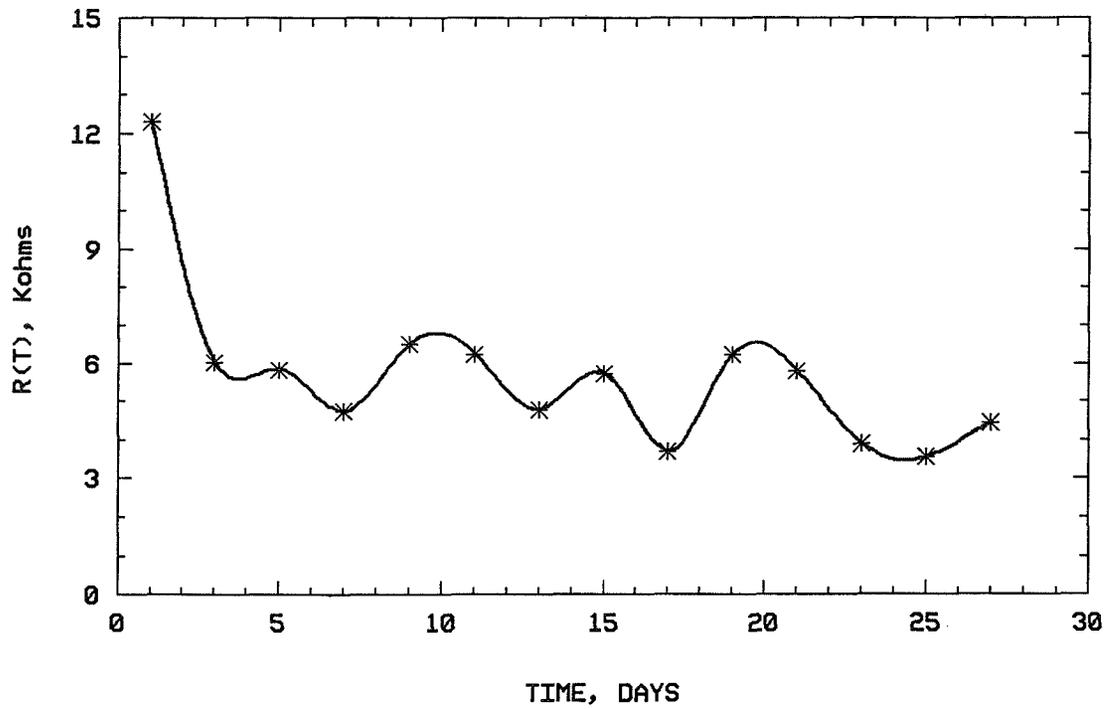


Figure 23. Charge transfer resistance, 2024-T3 Al, chromic acid anodize.

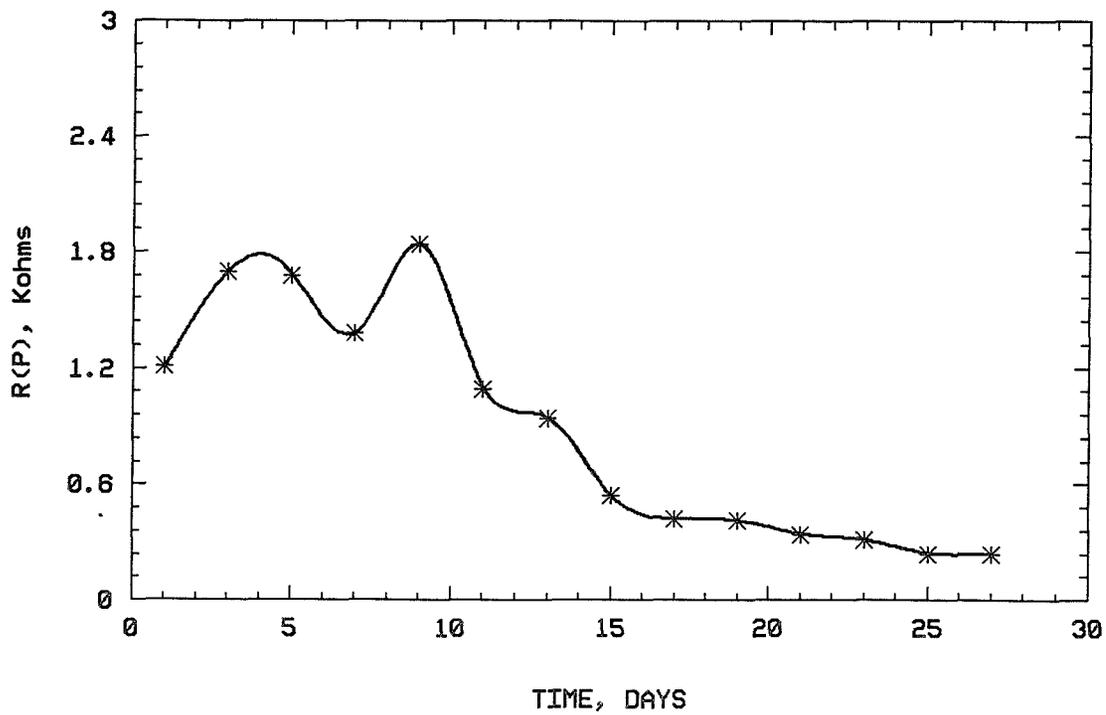


Figure 24. Pore resistance, 2024-T3 Al, chromic acid anodize.

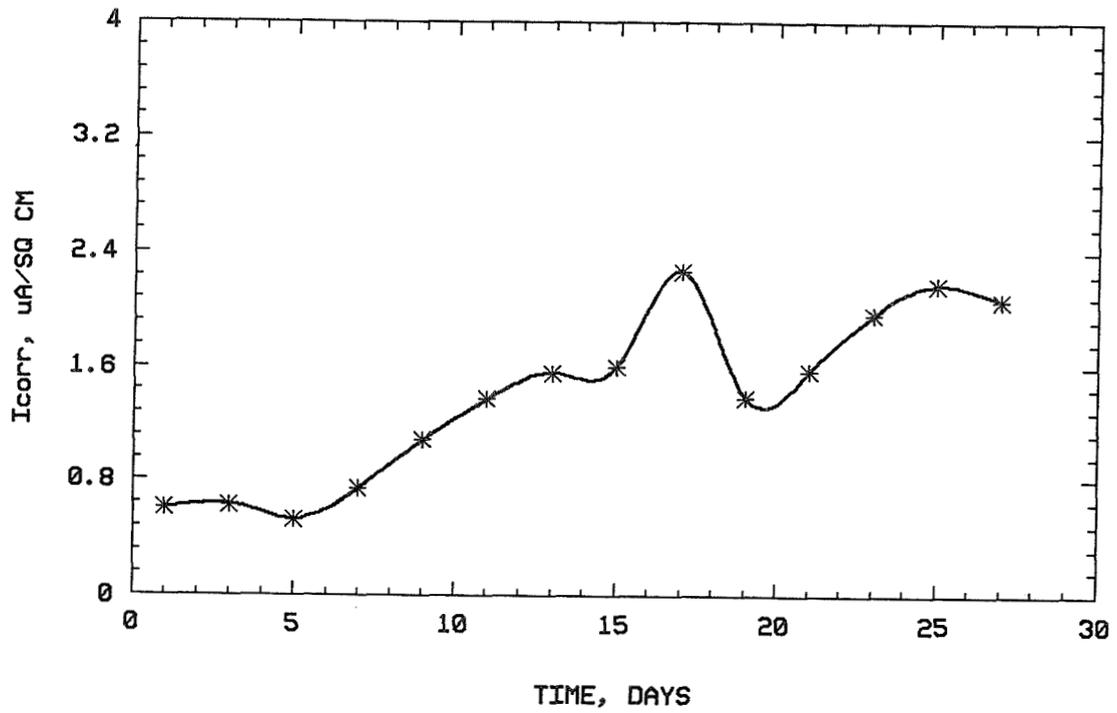


Figure 25. Corrosion current, 2024-T3 Al, chromic acid anodize.

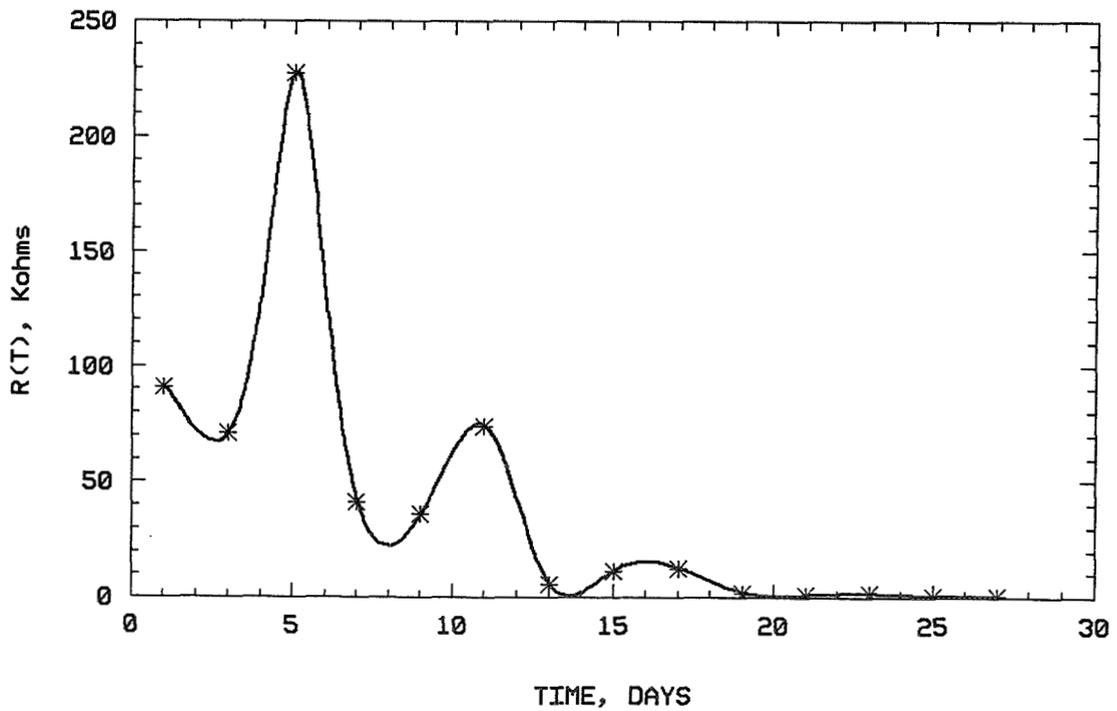


Figure 26. Charge transfer resistance, 2024-T3 Al, sulfuric acid anodize.

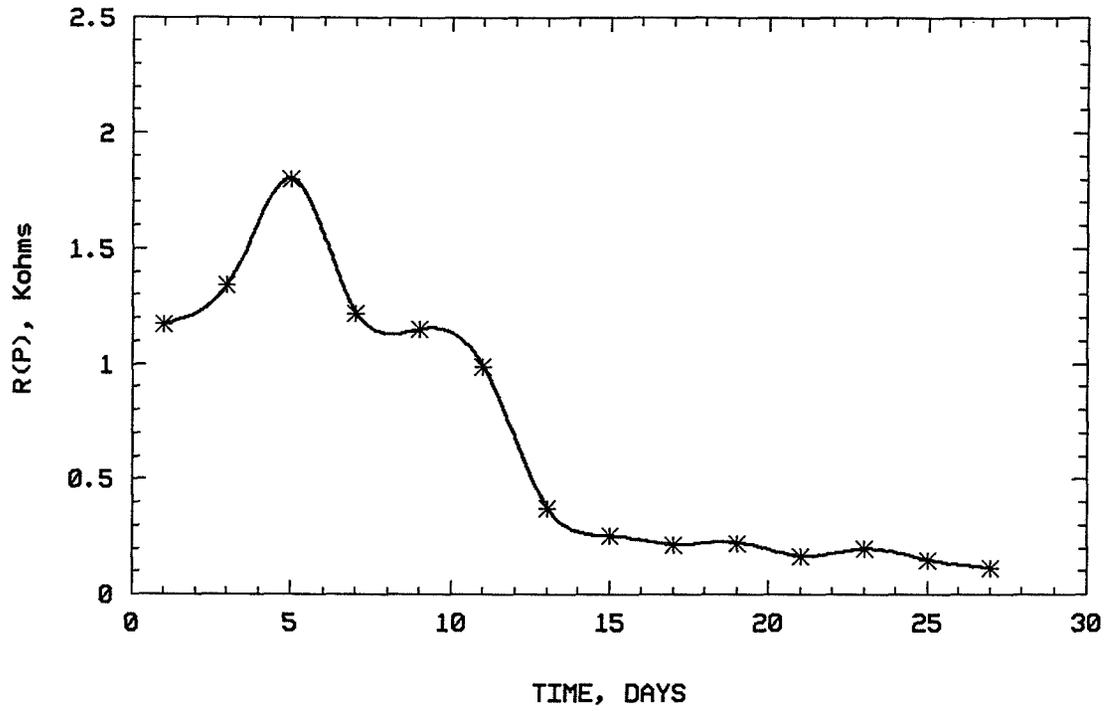


Figure 27. Pore resistance, 2024-T3 Al, sulfuric acid anodize.

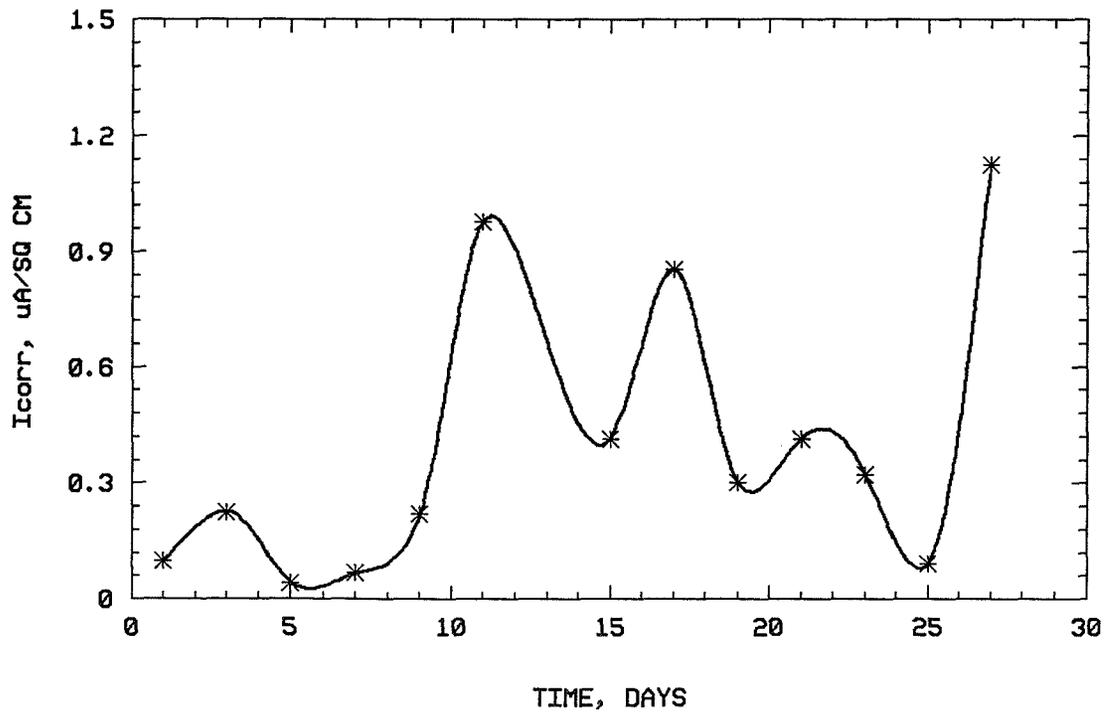


Figure 28. Corrosion current, 2024-T3 Al, sulfuric acid anodize.

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