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THE CORROSION PROTECTION OF 6061-T6 ALUMINUM BY A POLYURETHANE-SEALED ANODIZED COAT

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16. Abstract

The corrosion protection of 6061-T6 anodized aluminum afforded by a newly patented polyurethane seal has been studied using the ac impedance technique. Values of the average corrosion rates over a 27-day exposure period in 3.5% NaCl solutions at pH 5.2 and pH 9.5 compared very favorably for Lockheed-prepared polyurethane-sealed and dichromate-sealed coats of the same thickness. Average corrosion rates for both specimens over the first 7 days of exposure compared well with those for a hard anodized, dichromate-sealed coat, but rose well above those for the hard anodized coat over the entire 27-day period. This is attributed both to the greater thickness of the hard anodized coat, and possibly to its inherently better corrosion protective capability.

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INTRODUCTION

This work was undertaken to investigate the corrosion prevention afforded anodized aluminum by a newly patented invention which seals anodized aluminum in a hot water-borne polyurethane bath [1]. This procedure is of interest in connection with corrosion problems encountered in the water spray boiler on Ov-104, as well as with other aluminum corrosion problems.

The electrochemical ac impedance method was the primary investigative technique employed, with the dc polarization resistance being used where possible to corroborate values of the corrosion currents obtained with the ac impedance method. Since the samples used in these studies employed rather thin anodized coats, it was necessary to study dichromate-sealed specimens with about the same coating thickness for comparative purposes.

AC IMPEDANCE DATA ANALYSIS

Two equivalent circuit models were used for analysis of the ac impedance data, and are shown in figures 1 and 2. The model of figure 1 was the primary circuit model used in data analysis. The circuit model of figure 2 was used to calculate the effect of diffusion polarization. A contribution due to the Warburg impedance, or effect due to diffusion polarization, is given by

$$Z_{w} = \sigma\omega^{-1/2} - j\sigma\omega^{-1/2} \quad .$$

(1)

Here, Z_w is the Warburg impedance, $\omega = 2\pi \times$ frequency, $j = \sqrt{-1}$, and σ is the Warburg coefficient.

The value of σ is obtained using the model of figure 2, and, generally, the higher the value of σ, the less is the diffusion of the surrounding medium through the specimen coat. If the value of σ exceeds that of the charge transfer parameter R_t, the corrosion is diffusion controlled. Trends in σ-time curves usually correlate very well with positions of maxima and minima in the I_{CORR}-time curves, where I_{CORR} is the corrosion current, and with the trends in $R(P)$, the overall coating resistance.

Values for each of the circuit components in either figure 1 or figure 2 were treated as parameters in the nonlinear ORGLS [2] least squares program, which automatically adjusted these parameters to obtain a best fit to the observed bode magnitude data (log impedance versus log ω). Corrosion currents were calculated from ac impedance data using the relation:

$$I_{\text{CORR}} = \frac{(b_a) \times (b_c)}{2.303(b_a + b_c)} \cdot \frac{1}{R_t + R_f} , \tag{2}$$

which is the Stern-Geary equation for charge-transfer control [3–5]. Tafel constants (b_a and b_c) were estimated to be 50 mV each, and ($R_t + R_f$) is the total charge transfer resistance. The value of 50 mV each for the Tafel constants has been found to provide excellent agreement between values of I_{CORR} calculated by equation (2) and dc polarization resistance measurements [6]. The corrosion rate for 6061-T6 aluminum is given by [6]:

$$\text{Corrosion rate (mpy)} = 0.42635 \times I_{\text{CORR}} . \tag{3}$$

EXPERIMENTAL

Polyurethane-sealed and dichromate-sealed anodized aluminum samples were supplied by the Lockheed Aeronautical Systems Company. The samples were in the form of aluminum disks 1.43 cm (0.563 in) in diameter and approximately 0.16 cm (0.063 in) thick, coated on both sides with 7.6-μ to 12.7-μ (0.0003-in to 0.0005-in) thick sealed anodized coats. The sealing materials were either polyurethane or dichromate. Each specimen was sanded to bare metal on one side for electrical contact, then placed in the sample holder shown in figure 3. Sample surfaces were subsequently wiped with alcohol to remove fingerprints which would interfere with the experiments. The samples were immersed for 27 days in 3.5% NaCl solutions buffered at pH 5.2 and pH 9.5. The buffer solution for pH 5.2 consisted of 500 ml 0.1M potassium acid phthalate and 388 ml NaOH, with sufficient water added to make 1 liter of solution. The buffer solution for pH 9.5 contained 500 ml of 0.025M borax and 30 ml 0.1M HCl, with water added to make 1 liter of solution. Sufficient NaCl was added to each solution to obtain a 3.5% NaCl concentration. A saturated calomel reference electrode was used in all measurements.

AC impedance and dc polarization resistance measurements (where possible) were made on alternate days for the entire test period. The EG&G-PARC model 378 ac impedance system was used for the ac impedance measurements. These data were taken in three sections. The first two sections, beginning at 0.001 Hz and 0.1 Hz, respectively, were obtained using the fast Fourier transform technique. The last section, ranging from 5.1 to 80,000 Hz was collected using the lock-in amplifier technique. The sequencing was performed automatically using the autoexecute procedure, with all data being merged to a single set for each run. The period of collection for the ac impedance data was approximately 3 hours. After collection, the data were processed and analyzed with an IBM PC/AT computer, which also controlled the experiment, as shown in figures 1 and 2.

Data for the polarization resistance method were collected using the same system with the EG&G-PARC model 342C software, which was developed especially for dc measurements. The instrumentation developed by EG&G-PARC, automatically corrected the data during the scan for IR drop. The data were analyzed using the program POLCURR [7]. The theory for the polarization resistance technique has been described previously [8].

RESULTS AND DISCUSSION

Polyurethane-Sealed Aluminum

Magnified photographs of the surfaces of polyurethane-sealed anodized coats after 27 days of exposure at pH 5.2 and pH 9.5 are shown in figures 4 and 5. The sample exposed at pH 5.2 shows general corrosion over the entire exposed surface, with one large pit appearing in the upper right hand corner of figure 4. The sample exposed at pH 9.5 shows general corrosion over the entire surface, with several pits evident in figure 5.

Average corrosion rates over the first 7 days of exposure and after 27 days of exposure are listed in table 1 and compared to that for bare 6061-T6 aluminum, identified in table 2, measured on the first day of exposure. Results are compared to those for hard anodized, dichromate-sealed 6061-T6 aluminum, which had a much thicker anodized coat. The average corrosion rate for the polyurethane-sealed anodized coat compared very well to that obtained with the hard anodized, dichromate-sealed coat at pH 5.2 over the initial 7 days of exposure. Over the entire 27-day period, however, the average corrosion rate became greater than that for the hard anodized, dichromate-sealed sample. Curves for all parameters for the equivalent circuit models of figures 1 and 2 are shown in figures 6 through 13 for the polyurethane-sealed specimens. It may be seen from figure 9(a) that the corrosion current rose rapidly during the last few days of exposure for the polyurethane-sealed sample at pH 5.2, and, as a result, lead to the much higher value of the average corrosion rate observed for the 27-day period. Thus, the thickness of the anodized coat seems to be an important factor, with the much thicker hard anodized coat giving better corrosion protection over a longer period of time. The value of the major corrosion rate controlling parameter $R(T)$, shown in figure 7(c), reached a minimum value after about 7 days of exposure for the polyurethane-sealed sample, whereas the corresponding curve for the hard anodized coat reached a minimum value after 12 days of exposure [6]. However, the Warburg coefficient-time curve in figure 9(b) declined rather slowly when compared to that for the hard anodized, dichromate-sealed sample [6], which reached a minimum value after 10 days of exposure. Thus, diffusion of the surrounding medium through the polyurethane-sealed coat may be a bit slower than that for the hard anodized dichromate-sealed coat. Curves for the other model parameters for the polyurethane-sealed coat related very well to those for the charge transfer resistance and the Warburg coefficient-time curves.

The average corrosion rates for the polyurethane-sealed sample exposed at pH 9.5 are shown in table 1 for the first 7-day period and the entire 27-day period. The average corrosion rate for the first 7 days was greater than that for the corresponding sample at pH 5.2, but did not increase a great deal over the entire 27-day period. This is a result of the oscillating nature of the $R(T)$-time curve shown in figure 11(c), and is indicative of the healing effect previously observed at pH 9.5 [6]. The Warburg coefficient-time curve in figure 13(b) is similar to that observed at pH 5.2. The value of the corrosion rate for the first 7-day period was greater than that observed for hard anodized, dichromate-sealed 6061-T6 aluminum, and indicates that the corrosion protection by the polyurethane-sealed coat was better at pH 5.2 than at pH 9.5, contrary to results obtained for other anodized aluminum samples [6]. Values of the other parameter-time curves at pH 9.5 again correlate very well with those for the $R(T)$-time and Warburg coefficient-time curves, as for the polyurethane-sealed sample at pH 5.2. The fact that the average corrosion rates for the polyurethane-sealed sample at pH 9.5 were greater than those for the hard anodized, dichromate-sealed sample is attributed to the relative thinness of the polyurethane-sealed coat, although a possible increased effectiveness due to hard anodizing might be indicated.

Dichromate-Sealed Aluminum

The study of dichromate-sealed samples prepared by Lockheed provided a direct comparison of these samples with those for hard anodized, dichromate-sealed samples. The coating thickness for the Lockheed-prepared samples was much less than that for the hard anodized samples, and was the same as that for the Lockheed-prepared polyurethane-sealed samples. The difference in coating thickness must therefore be taken into account.

Photographs of the surfaces of samples exposed at pH 5.2 and pH 9.5 are shown in figures 14 and 15. General corrosion over the whole surface appears to be less at pH 5.2 than at pH 9.5. However, large pits are evident at pH 5.2, as shown in figure 14, whereas only slight pitting occurs at pH 9.5.

The average corrosion rate for the dichromate-sealed anodized aluminum was slightly less than that for the hard anodized sample at pH 5.2 over the first 7-day period, but rose more rapidly during the remaining exposure time than did that for the hard anodized specimen. Curves for parameter-time results are shown in figures 16 through 18 for pH 5.2. Warburg-coefficient-time curves could not be satisfactorily obtained at either pH for the dichromate-sealed samples. The corrosion current-time curve at pH 5.2 is shown in figure 18(c) and indicated that the corrosion rate, although oscillating, rose rather rapidly during the latter part of the exposure period.

The rate-controlling parameter $R(T)$ reached a minimum after 10 days of exposure, which was slightly longer than that for the polyurethane-sealed sample at pH 5.2 (7 days) and comparable to that for the hard anodized sample [6]. Parameter-time curves for other parameters generally followed expected trends.

The average corrosion rate for the first 7-day period at pH 9.5 was comparable to that for the thicker hard anodized sample, but again rose to a larger value over the entire exposure period. Parameter-time variations are shown in figures 19 through 21 for samples exposed at pH 9.5. The $R(T)$-time curve in figure 20(c) indicates a minimum value after 10 days, comparable to the result

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obtained at pH 5.2. The average corrosion rates at both pH 5.2 and pH 9.5 are comparable to those for the polyurethane-sealed samples over the entire 27 days exposure period, but are larger than those for the hard anodized dichromate-sealed samples. Again, this may be attributed to the greater thickness of the hard anodized sample, and, possibly to a greater effectiveness of hard anodizing in corrosion prevention. The I_{CORR}-time curve in figure 21(c) again illustrates the healing effect at pH 9.5. This may possibly be due to a build-up of corrosion products at pH 9.5, a probable result of the lesser solubility of the corrosion products.

CONCLUSIONS

The parameter-time curves for the equivalent circuit models of the ac impedance technique generally followed expected trends. Resistance-time curves generally decrease in value with time, while capacitance-time curves generally increased, indicating a decrease in the effective thickness of the capacitors.

Average corrosion rates for the first 7 days of exposure for the Lockheed-prepared specimens generally compared favorably with those for hard anodized, dichromate-sealed specimens with a much greater thickness. The average corrosion rates over the first 7 days were compared because of the difference in thickness, the hard anodized, dichromate-sealed coatings being 45.7 microns thick, whereas both the polyurethane and dichromate-sealed coated samples from Lockheed were only 10.2 microns thick. However, over the extended 27-day period of exposure, the average corrosion rates of the thinner polyurethane-sealed and dichromate-sealed samples were higher than those for the hard anodized, dichromate-sealed samples. This effect may have been due to the thinner coats on the Lockheed samples, but the greater effectiveness of the hard anodizing tech-nique in corrosion protection could have been a factor.

Values of the average corrosion rates over the entire 27-day period compared very favorably for the Lockheed polyurethane-sealed and dichromate-sealed coats. The diffusion process was shown to have been slowed by the polyurethane seal, and the polyurethane seal was much more effective at pH 5.2 than at pH 9.5, contrary to the results obtained for other anodized coatings.

RECOMMENDATIONS

It is suggested that the polyurethane seal be combined with the hard anodizing method and that the coating thickness be increased, possibly providing greater corrosion protection.
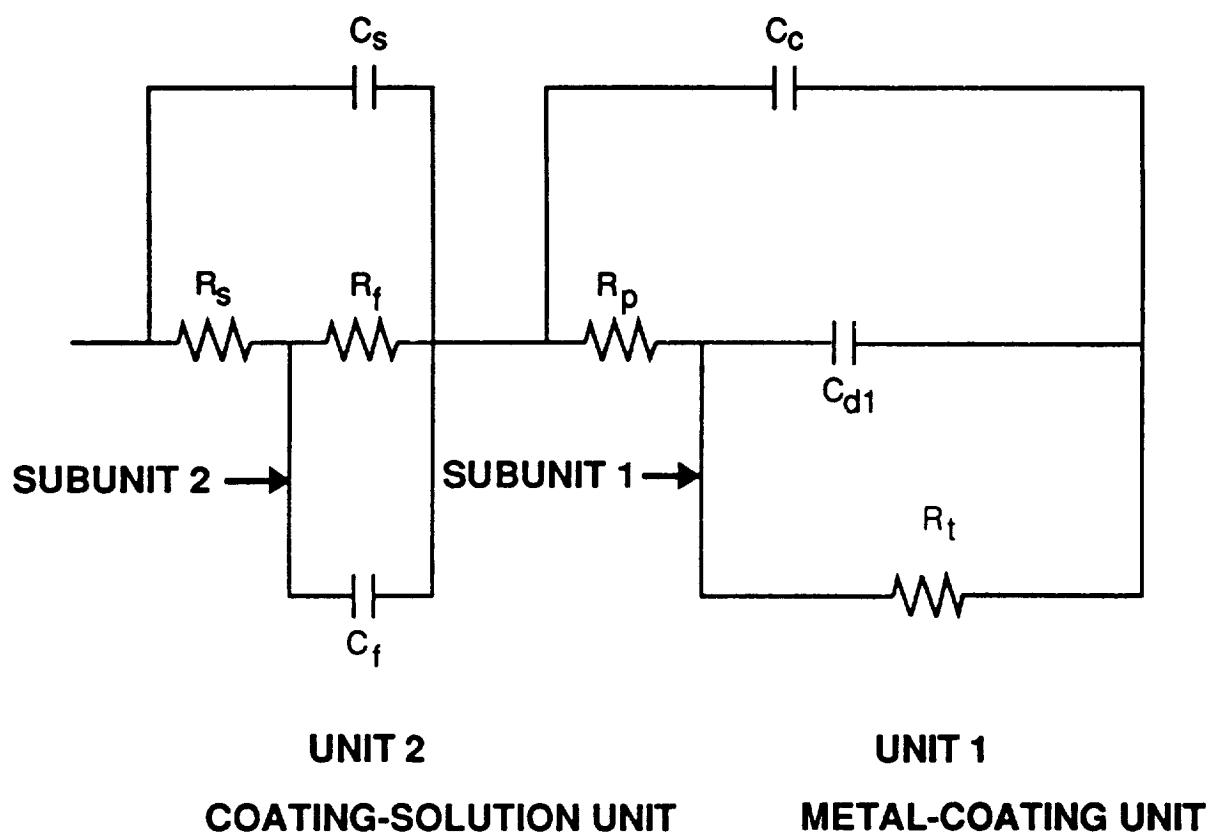
C_s SOLUTION CAPACITANCE

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

Figure 1. Circuit representing ac impedance response for anodized aluminum.
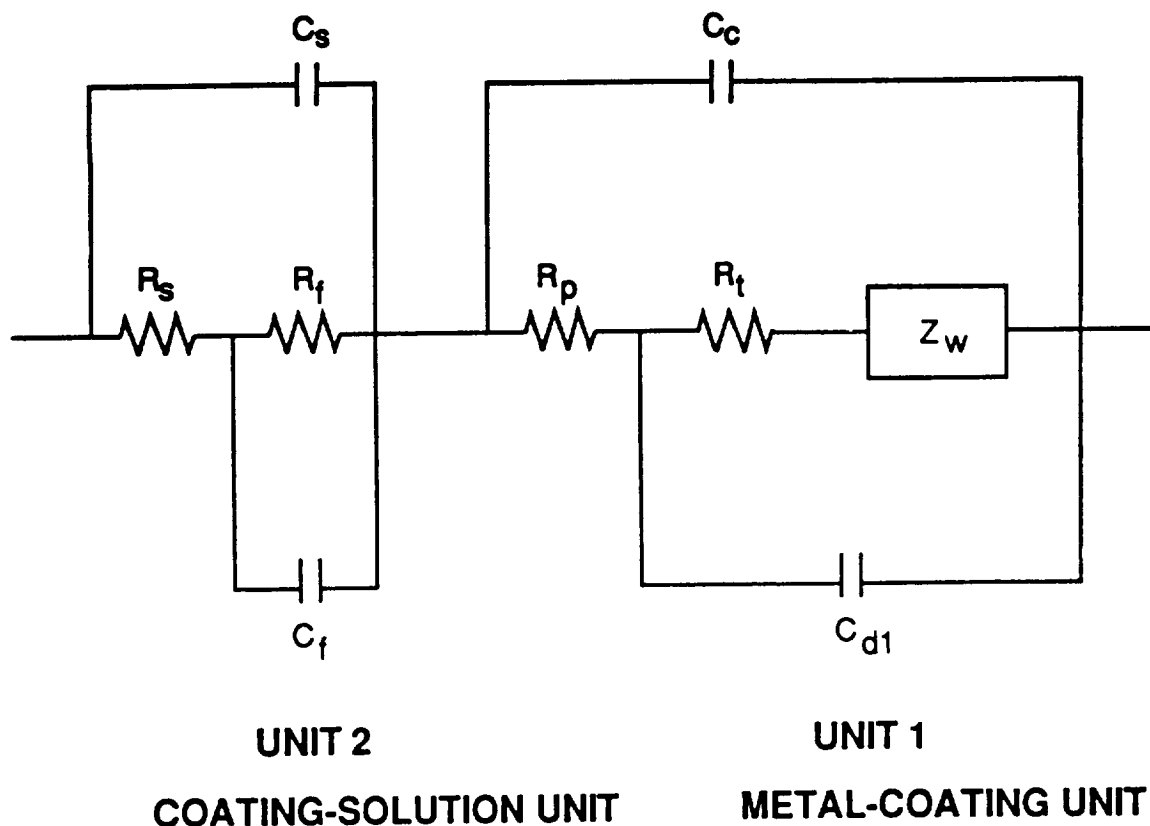
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UNIT 2

COATING-SOLUTION UNIT

UNIT 1

METAL-COATING UNIT

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)

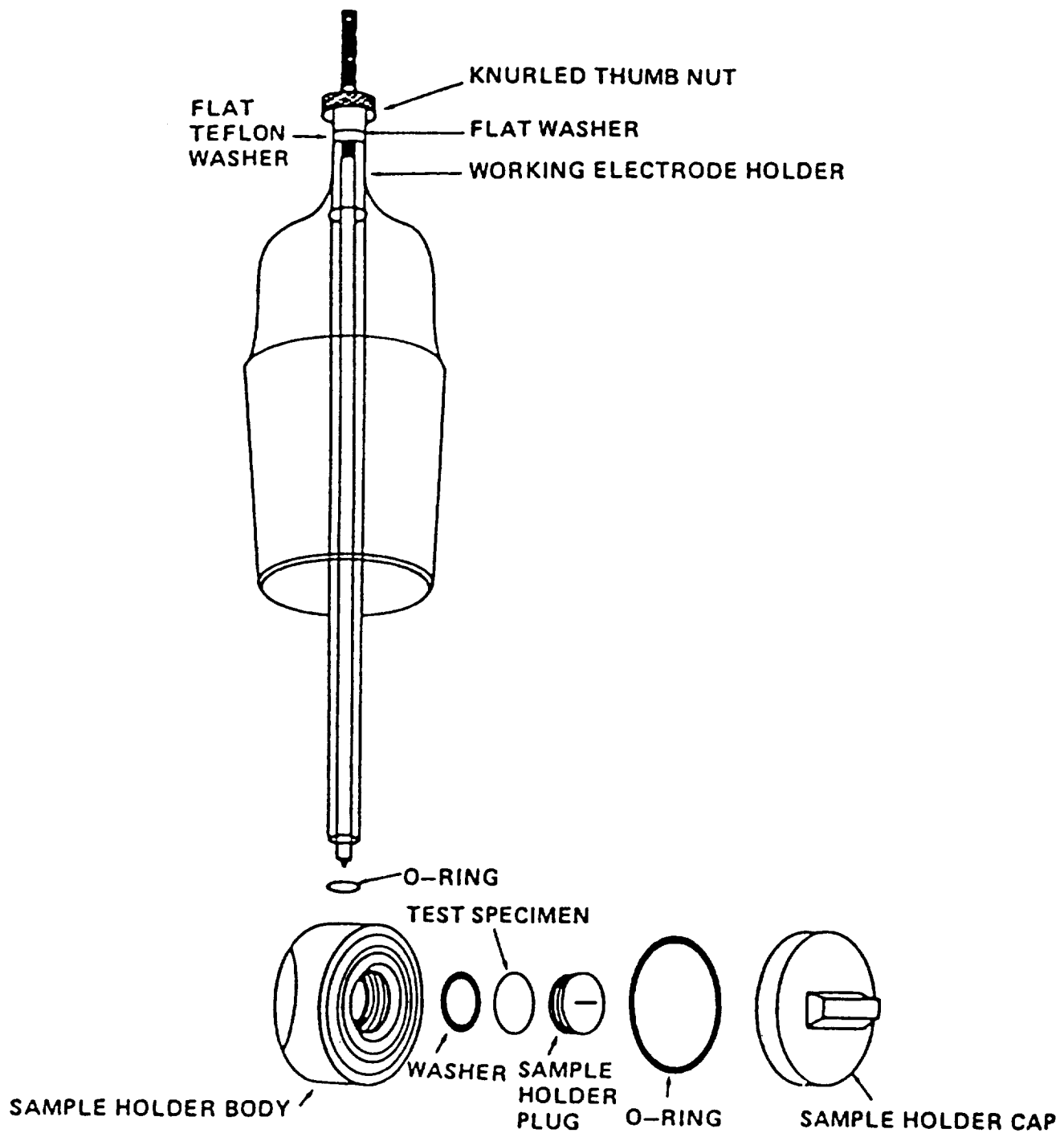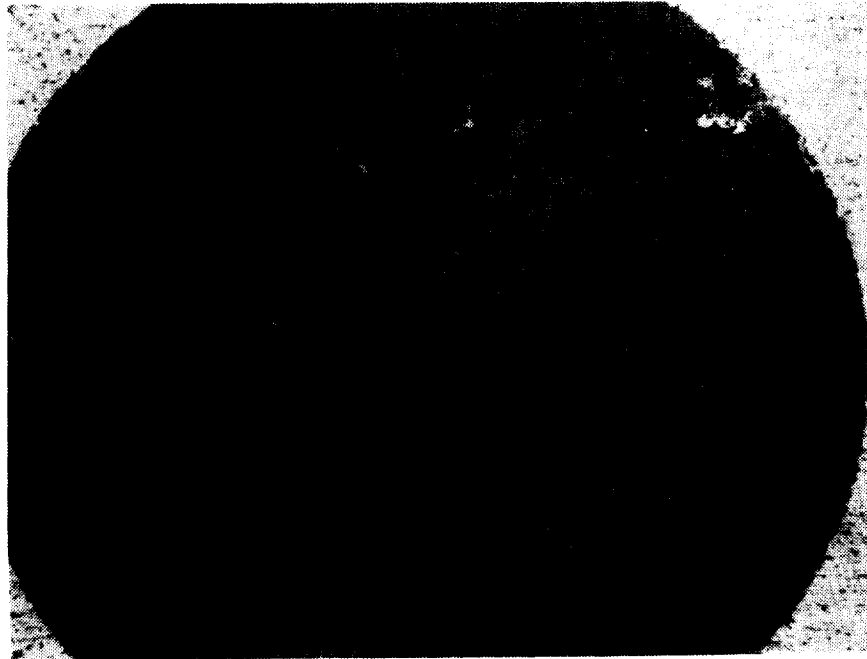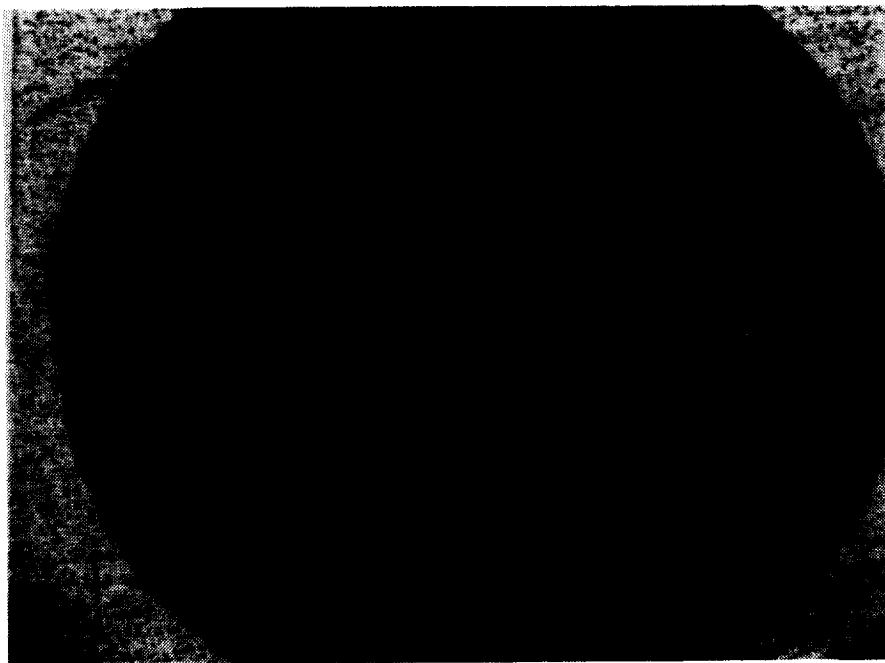Figure 2. AC impedance response including Warburg impedance.

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Figure 3. Exploded view of the sample holder.

10X

Figure 4. Top view of polyurethane-sealed sample exposed to 3.5% NaCl solution at pH 5.2.

10X

Figure 5. Top view of polyurethane-sealed sample exposed to 3.5% NaCl solutions at pH 9.5.
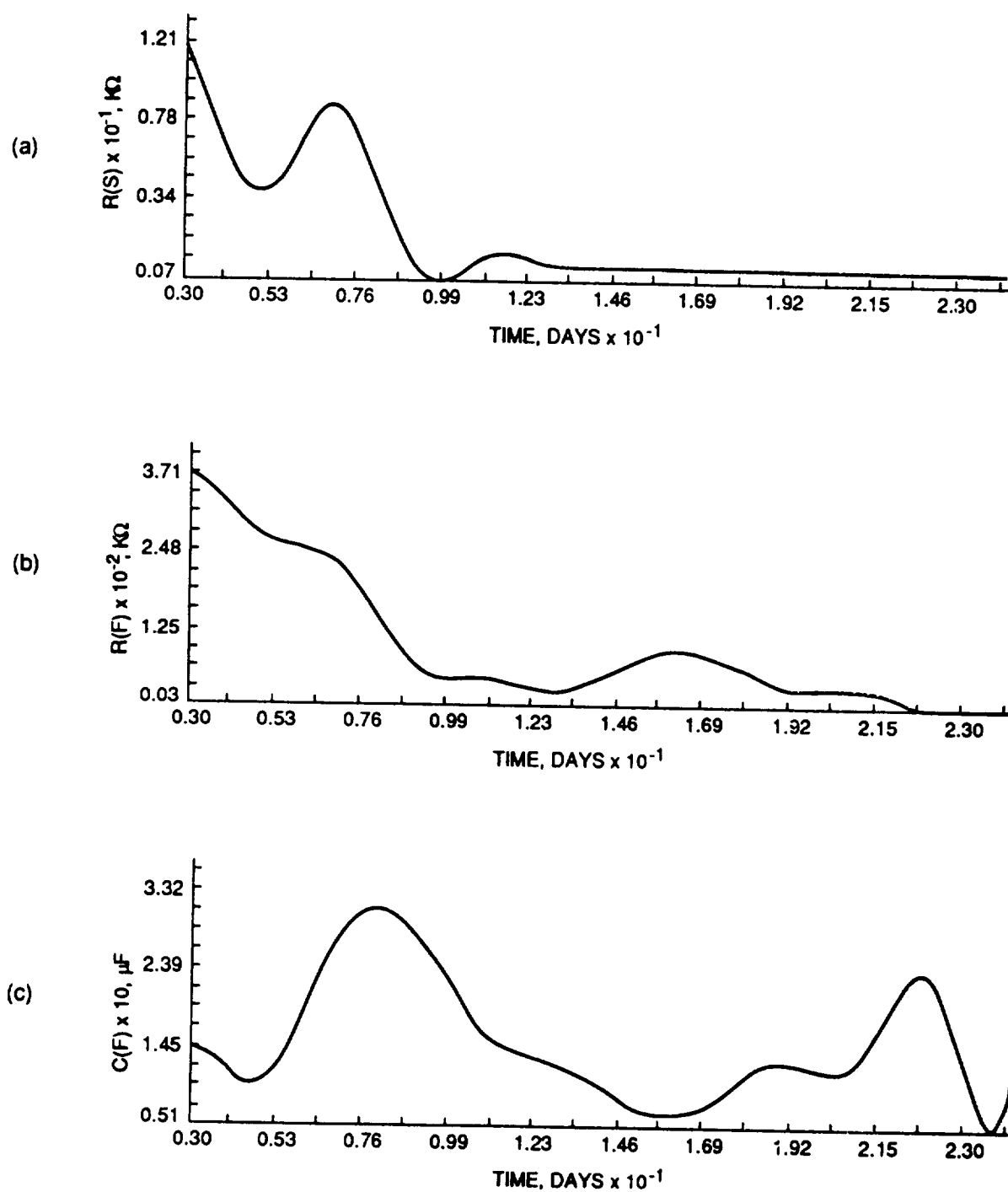
POLYURETHANE SEALED
pH 5.2

(a)

(b)

(c)

Figure 6. R(S)-, R(F)-, and C(F)-time curves for polyurethane seal at pH 5.2.
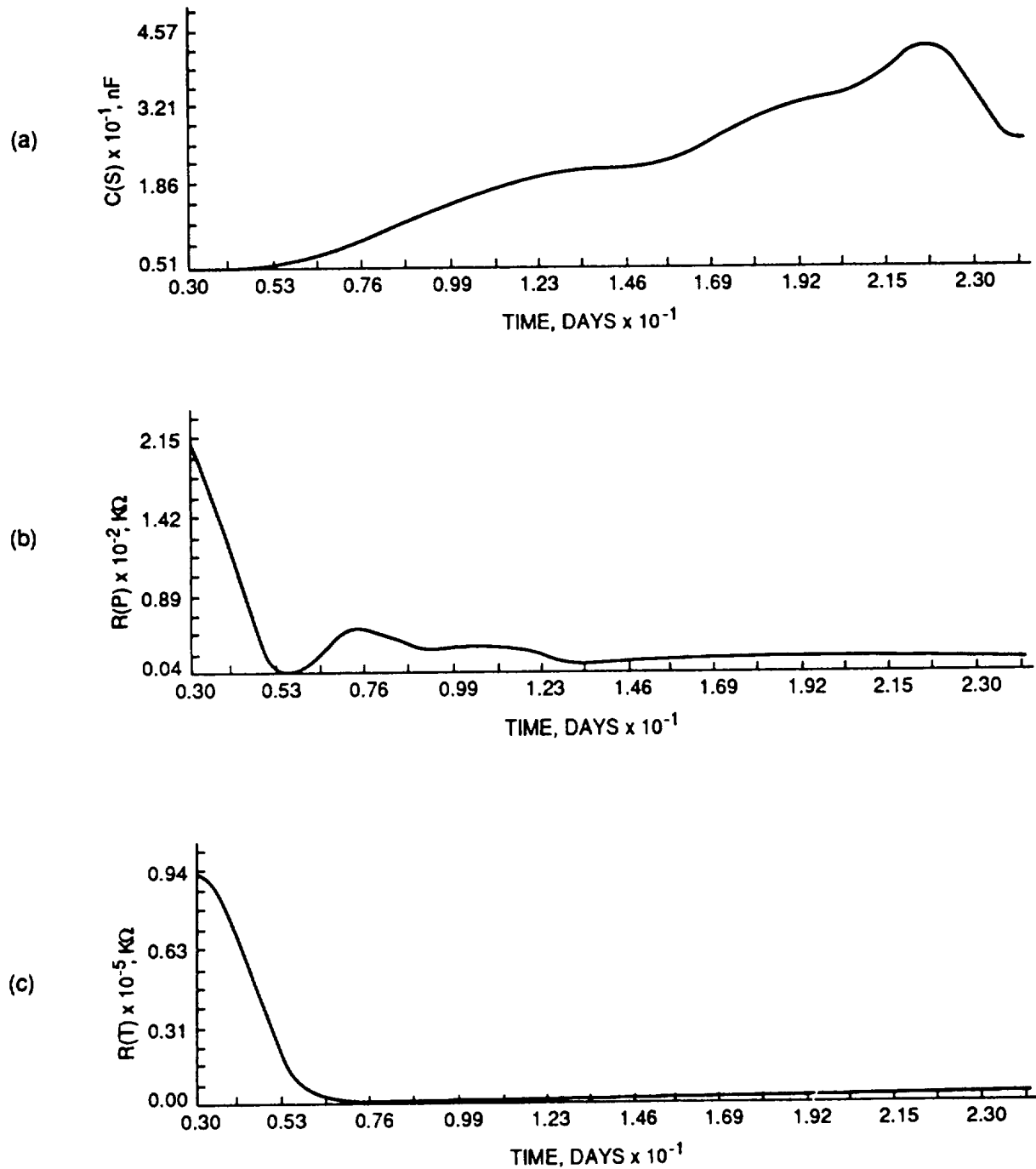
10

POLYURETHANE SEALED
pH 5.2

(a)

(b)

(c)

Figure 7. C(S)-, R(P)-, and R(T)-time curves for polyurethane seal at pH 5.2.

POLYURETHANE SEALED
pH 5.2

(a)

C(DL), μ F

2.02

1.48

0.94

0.39

0.30 0.53 0.76 0.99 1.23 1.46 1.69 1.92 2.15 2.30

TIME, DAYS x 10⁻¹

(b)

C(c)x10⁻², nF

0.96

0.67

0.38

0.09

0.30 0.53 0.76 0.99 1.23 1.46 1.69 1.92 2.15 2.38
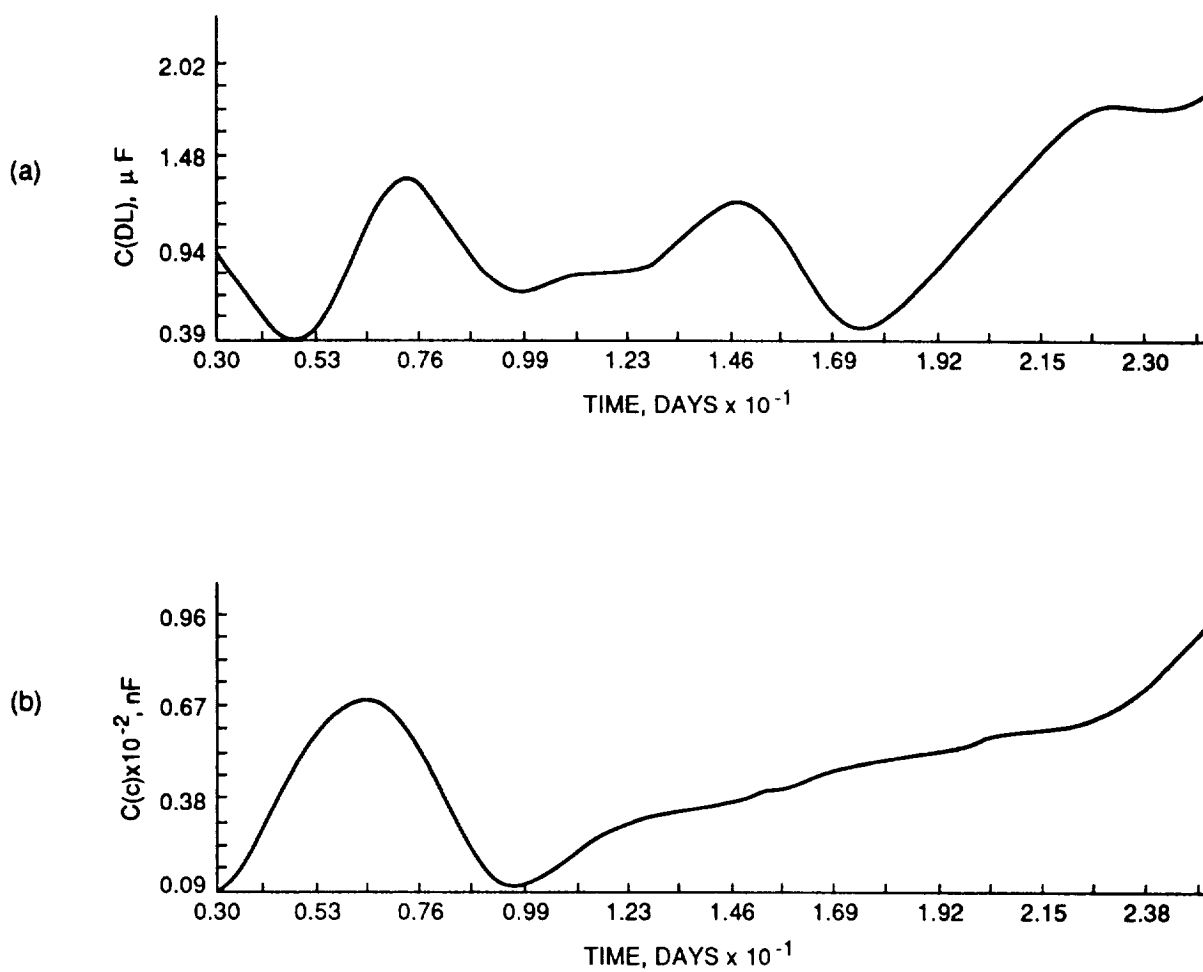
TIME, DAYS x 10⁻¹

Figure 8. C(DL)- and C(C)-time curves for polyurethane seal at pH 5.2.

12
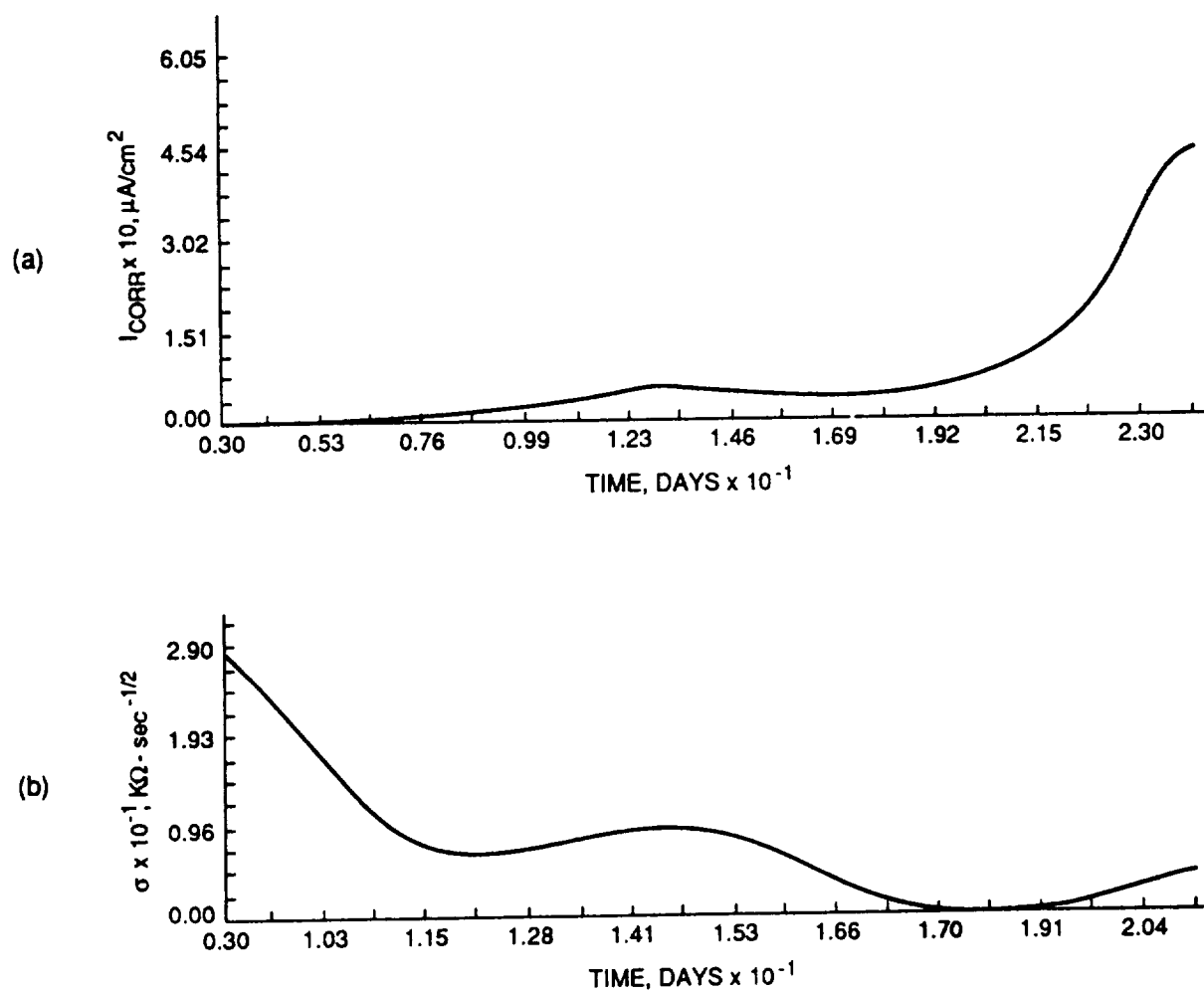
POLYURETHANE SEALED
pH 5.2

(a)

(b)

Figure 9. I_{CORR} and Warburg coefficient-time curves for polyurethane seal at pH 5.2.
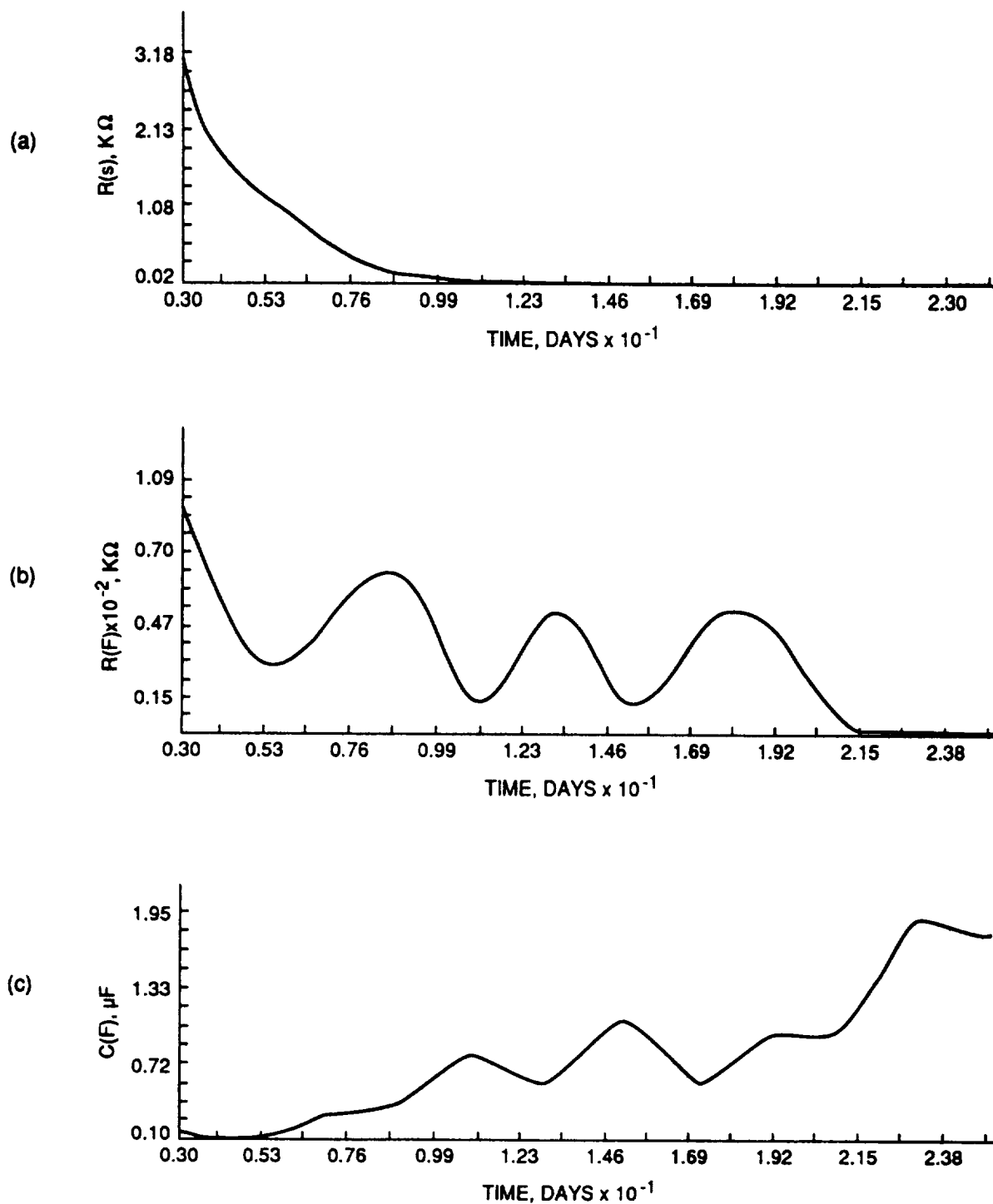
13

POLYURETHANE SEALED
pH 9.5

Figure 10. R(S)-, R(F)-, and C(F)-time curves for polyurethane seal at pH 9.5.
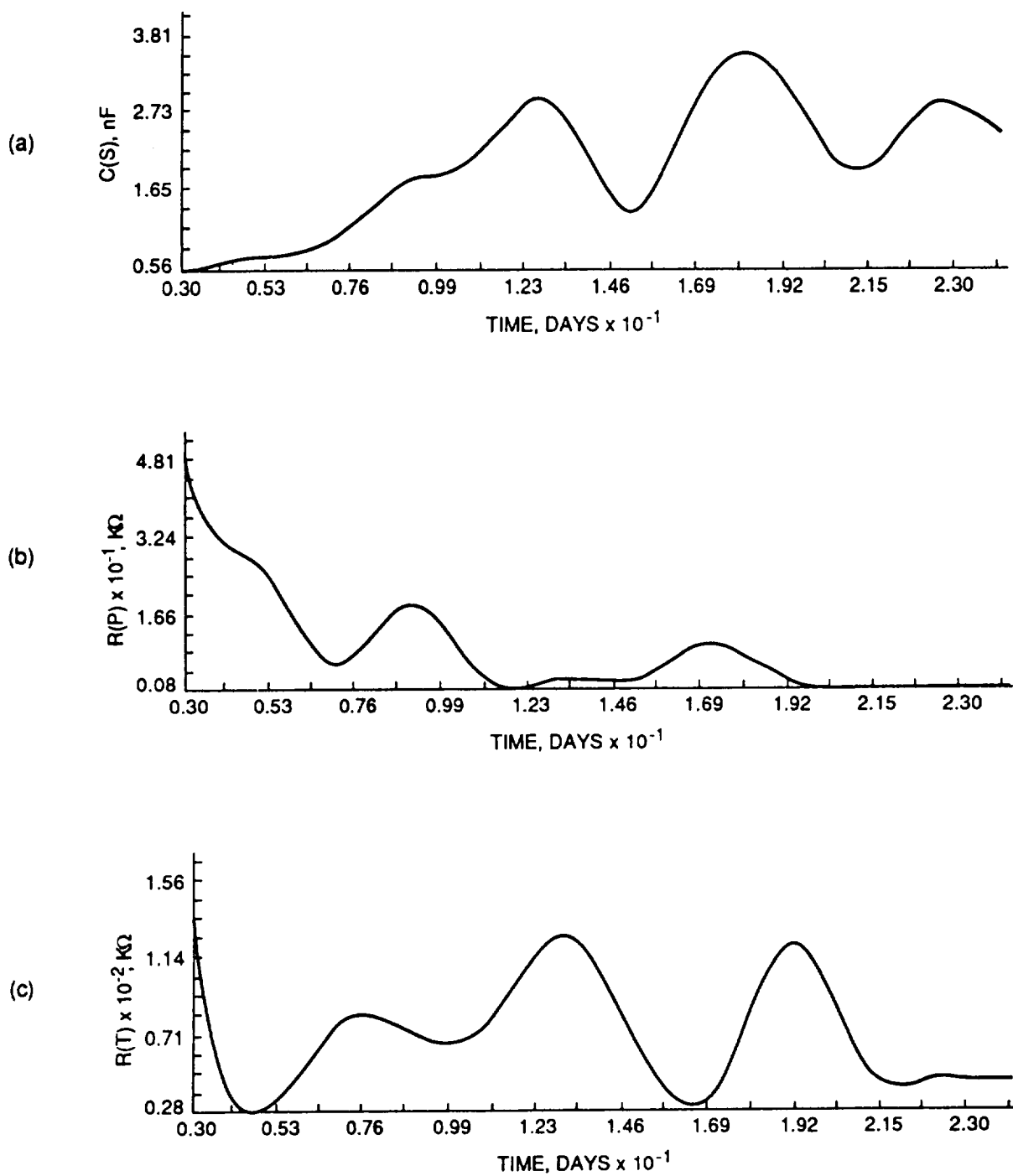
14

POLYURETHANE SEALED
pH 9.5

(a)

(b)

(c)

Figure 11. C(S)-, R(P)-, and R(T)-time curves for polyurethane seal at pH 9.5.

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POLYURETHANE SEALED
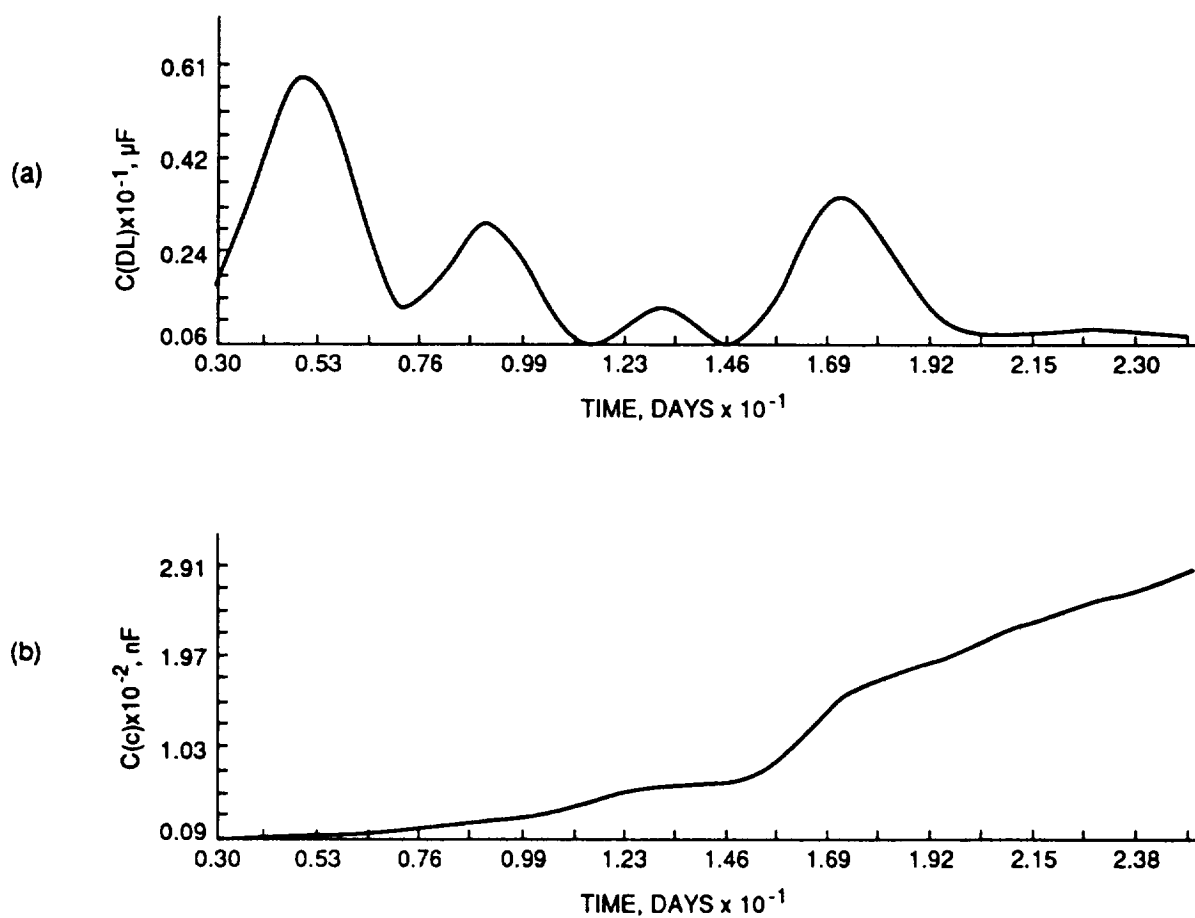## pH 9.5

(a)

(b)

Figure 12. C(DL)- and C(C)-time curves for polyurethane seal at pH 9.5.

16

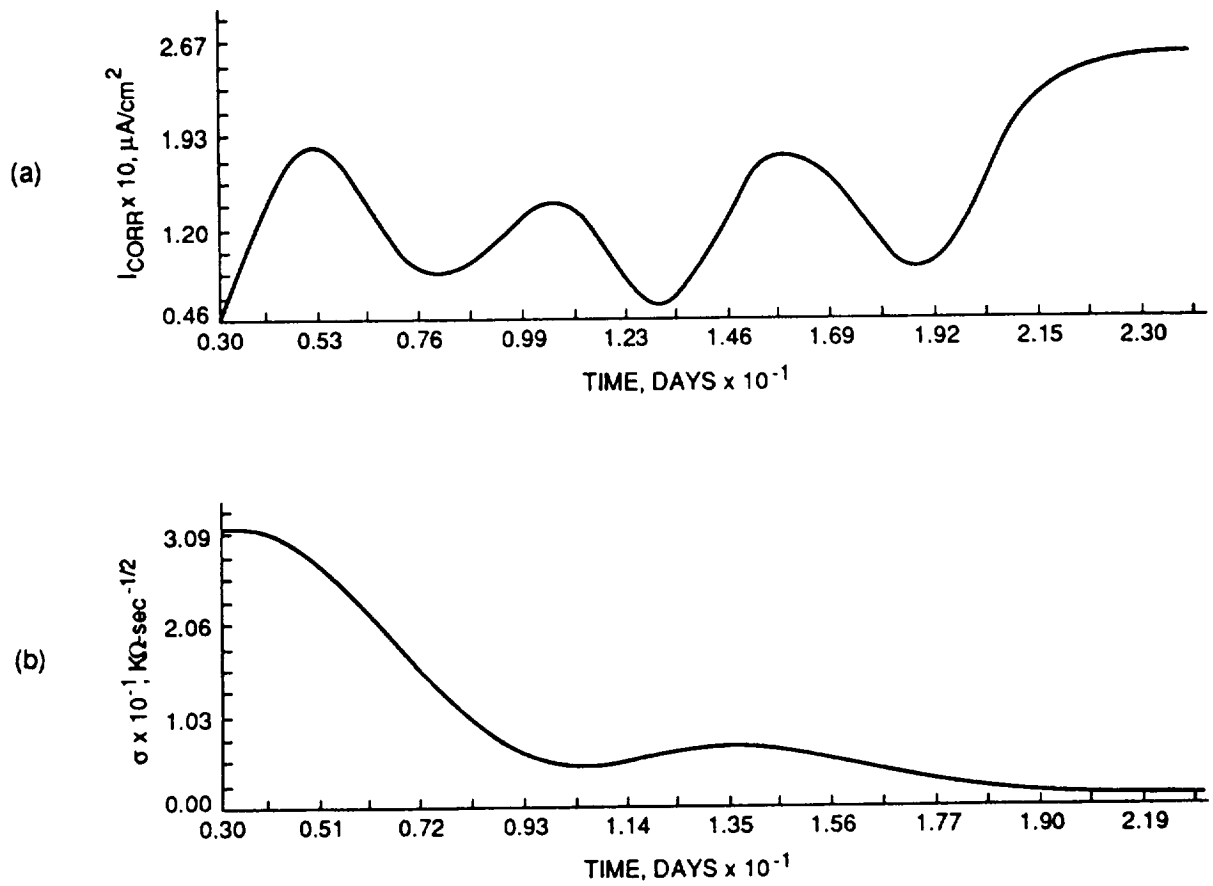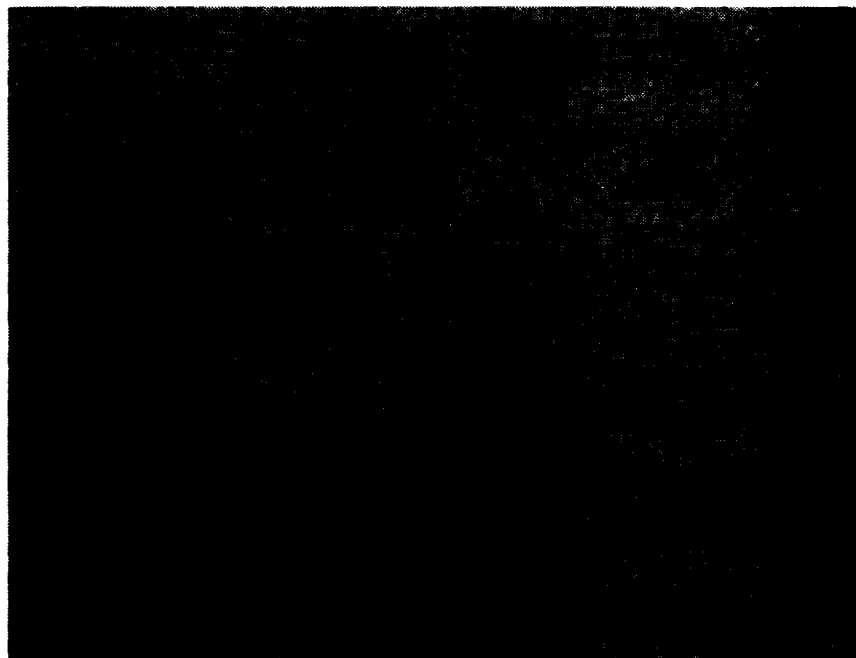# POLYURETHANE SEALED
pH 9.5

(a)

(b)

Figure 13. I_{CORR} and Warburg coefficient-time curves for polyurethane seal at pH 9.5.

10X

Figure 14. Top view of dichromate-sealed sample exposed to 3.5% NaCl solution at pH 5.2.

10X

Figure 15. Top view of dichromate-sealed sample exposed to 3.5% NaCl solution at pH 9.5.
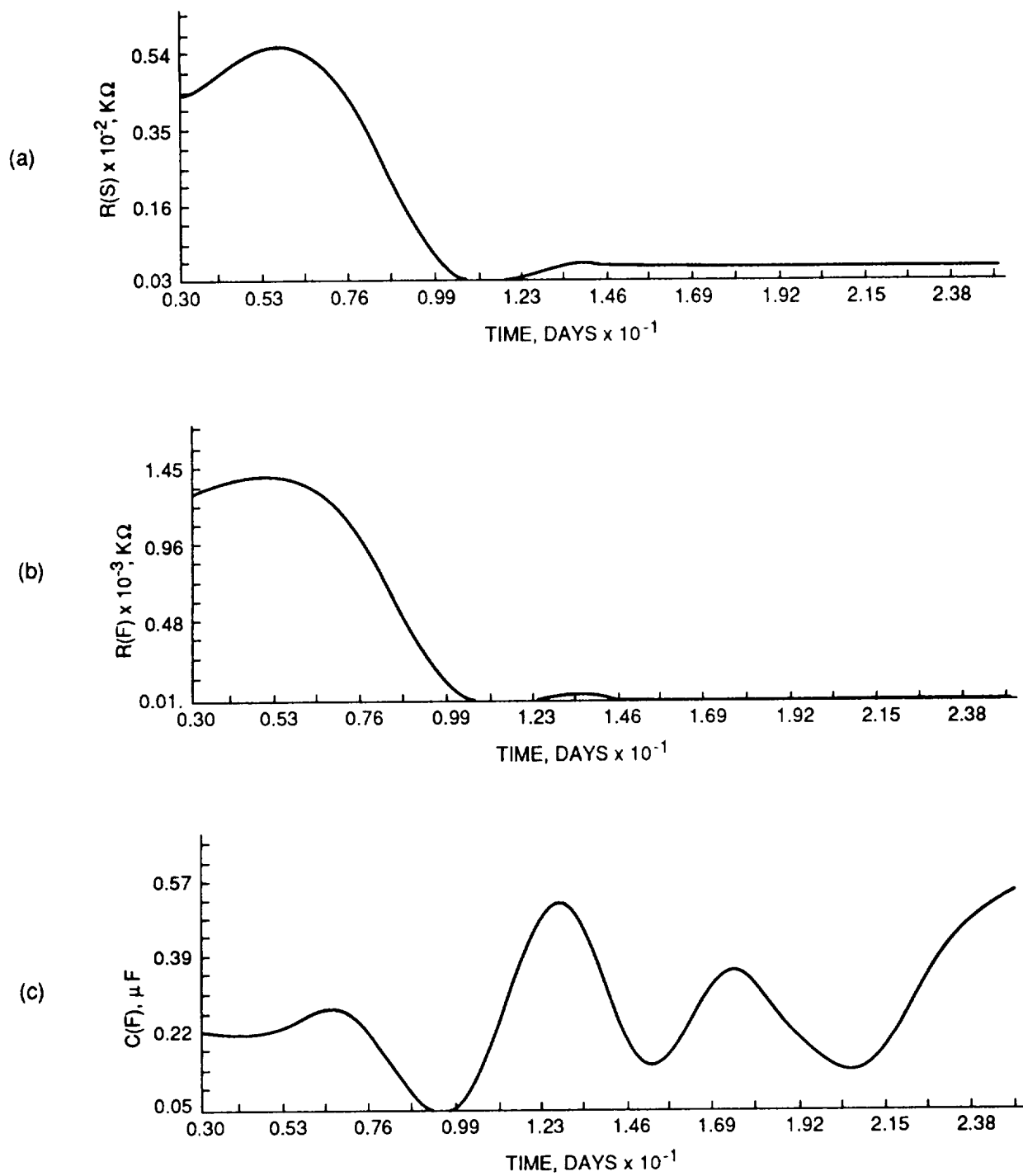
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DICHROMATE SEALED
pH 5.2

(a)

R(S) x 10⁻², KΩ axis values: 0.54, 0.35, 0.16, 0.03

TIME, DAYS x 10⁻¹ axis values: 0.30, 0.53, 0.76, 0.99, 1.23, 1.46, 1.69, 1.92, 2.15, 2.38

(b)

R(F) x 10⁻³, KΩ axis values: 1.45, 0.96, 0.48, 0.01

TIME, DAYS x 10⁻¹ axis values: 0.30, 0.53, 0.76, 0.99, 1.23, 1.46, 1.69, 1.92, 2.15, 2.38

(c)

C(F), µF axis values: 0.57, 0.39, 0.22, 0.05

TIME, DAYS x 10⁻¹ axis values: 0.30, 0.53, 0.76, 0.99, 1.23, 1.46, 1.69, 1.92, 2.15, 2.38

Figure 16. R(S)-, R(F)-, and C(F)-time curves for dichromate seal at pH 5.2.

DICHROMATE SEALED
pH 5 2

(a)

(b)

(c)
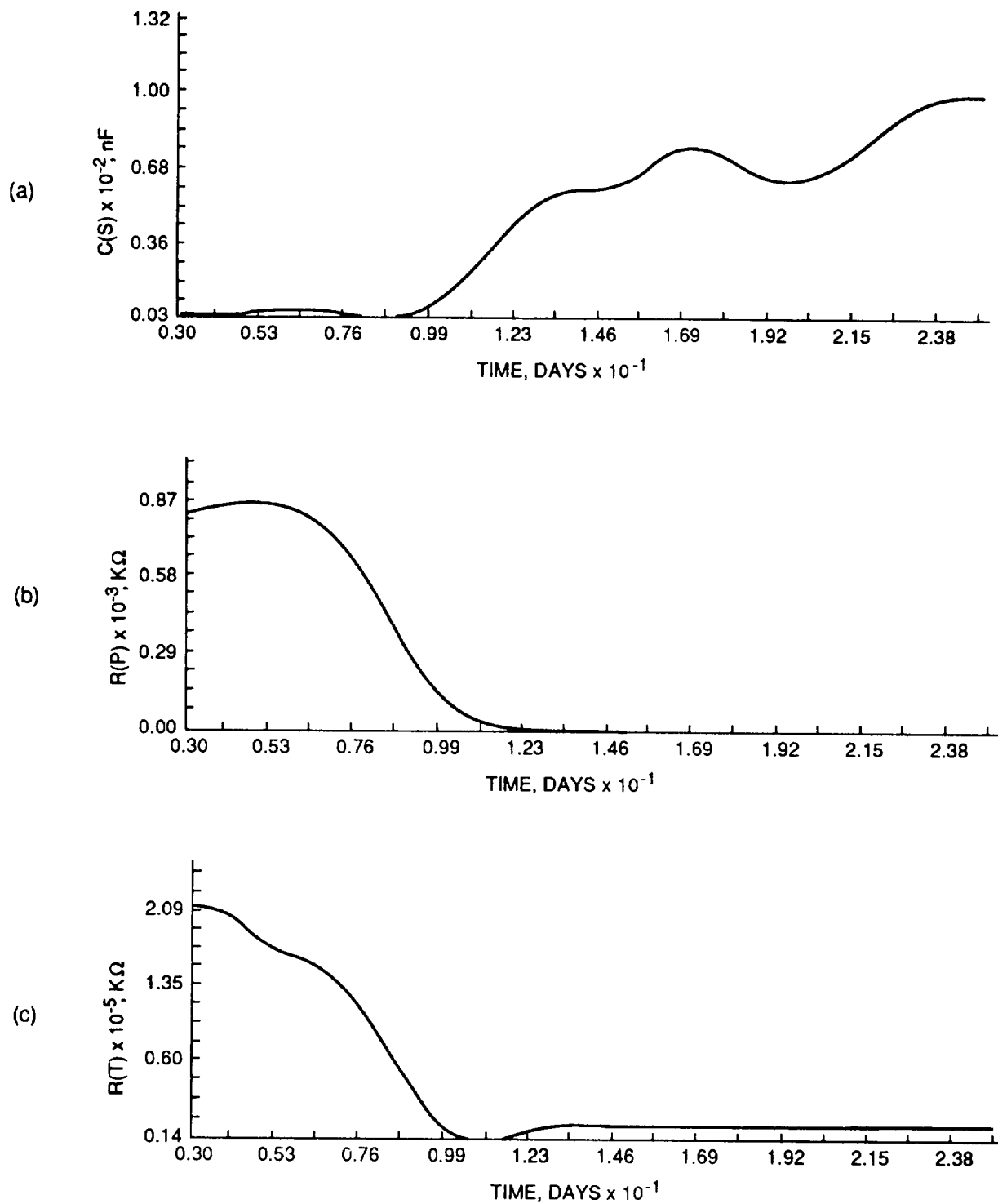
Figure 17. C(S)-, R(P)-, and R(T)-time curves for dichromate seal at pH 5.2.

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DICHROMATE SEALED
pH 5.2

(a)

C(DL), μF

4.75

3.15

1.56

0.04

0.30 0.53 0.76 0.99 1.23 1.46 1.69 1.92 2.15 2.38

TIME, DAYS x 10⁻¹

(b)

C(C) x 10⁻², nF

1.27

0.87

0.48

0.09

0.30 0.53 0.76 0.99 1.23 1.46 1.69 1.92 2.15 2.38

TIME, DAYS x 10⁻¹

(c)

I_{CORR} x 10, μ A/cm²

3.20

2.12

1.04

0.04

0.30 0.53 0.76 0.99 1.23 1.46 1.69 1.92 2.15 2.38
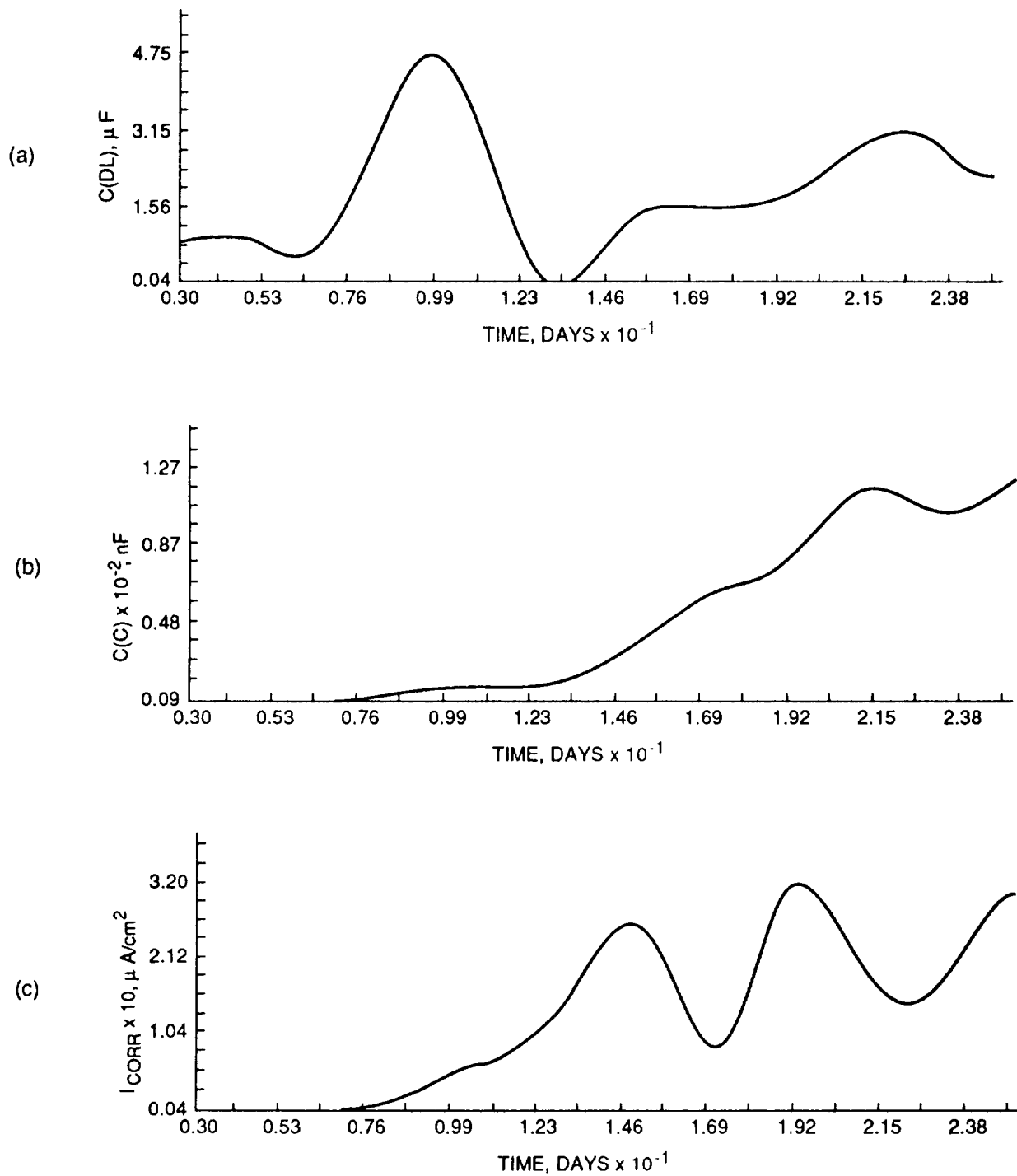
TIME, DAYS x 10⁻¹

Figure 18. C(DL)-, C(C)-, and I_{CORR}-time curves for dichromate seal at pH 5.2.
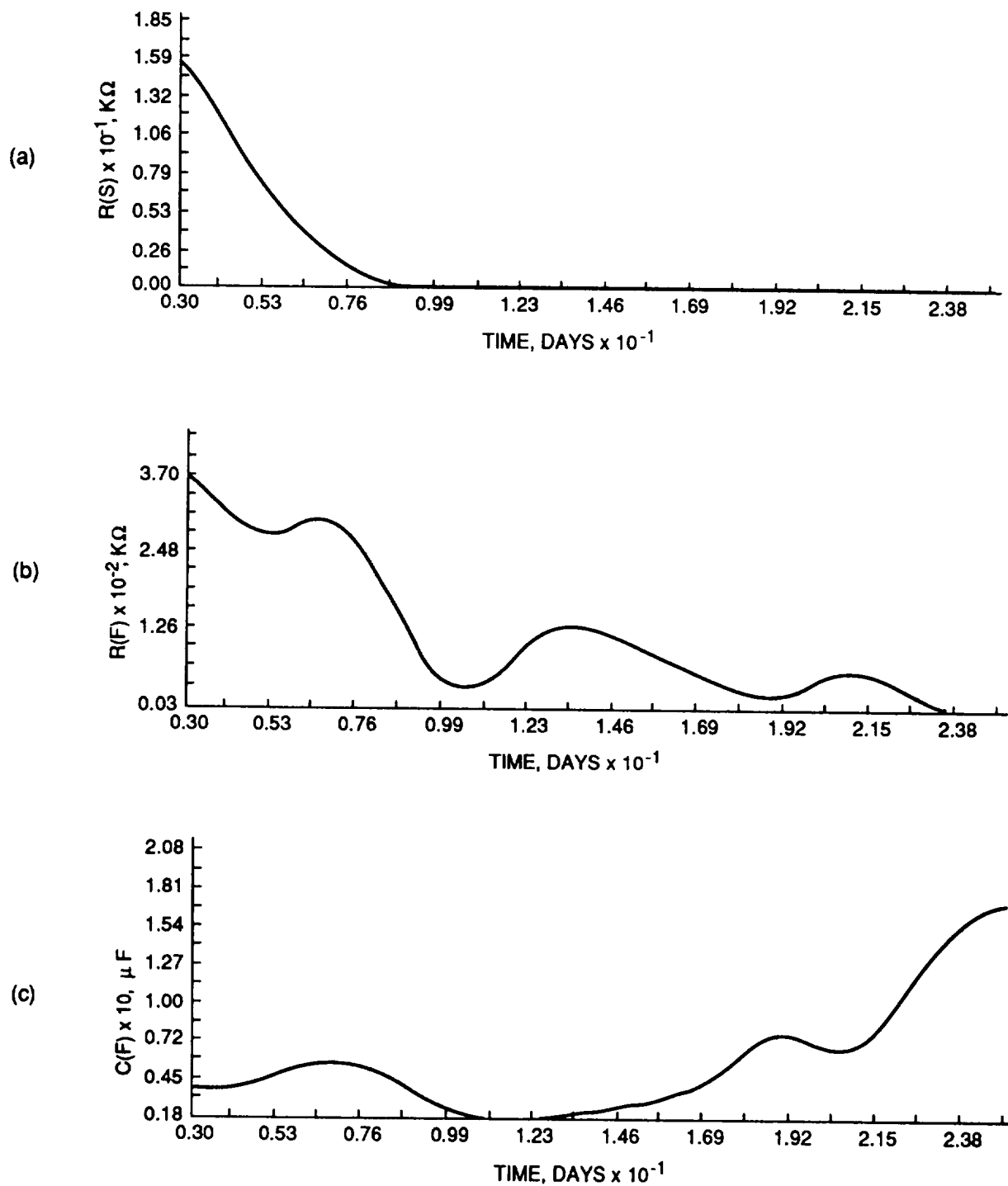
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DICHROMATE SEALED
pH 9.5

Figure 19. R(S)-, R(F)-, and C(F)-time curves for dichromate seal at pH 9.5.
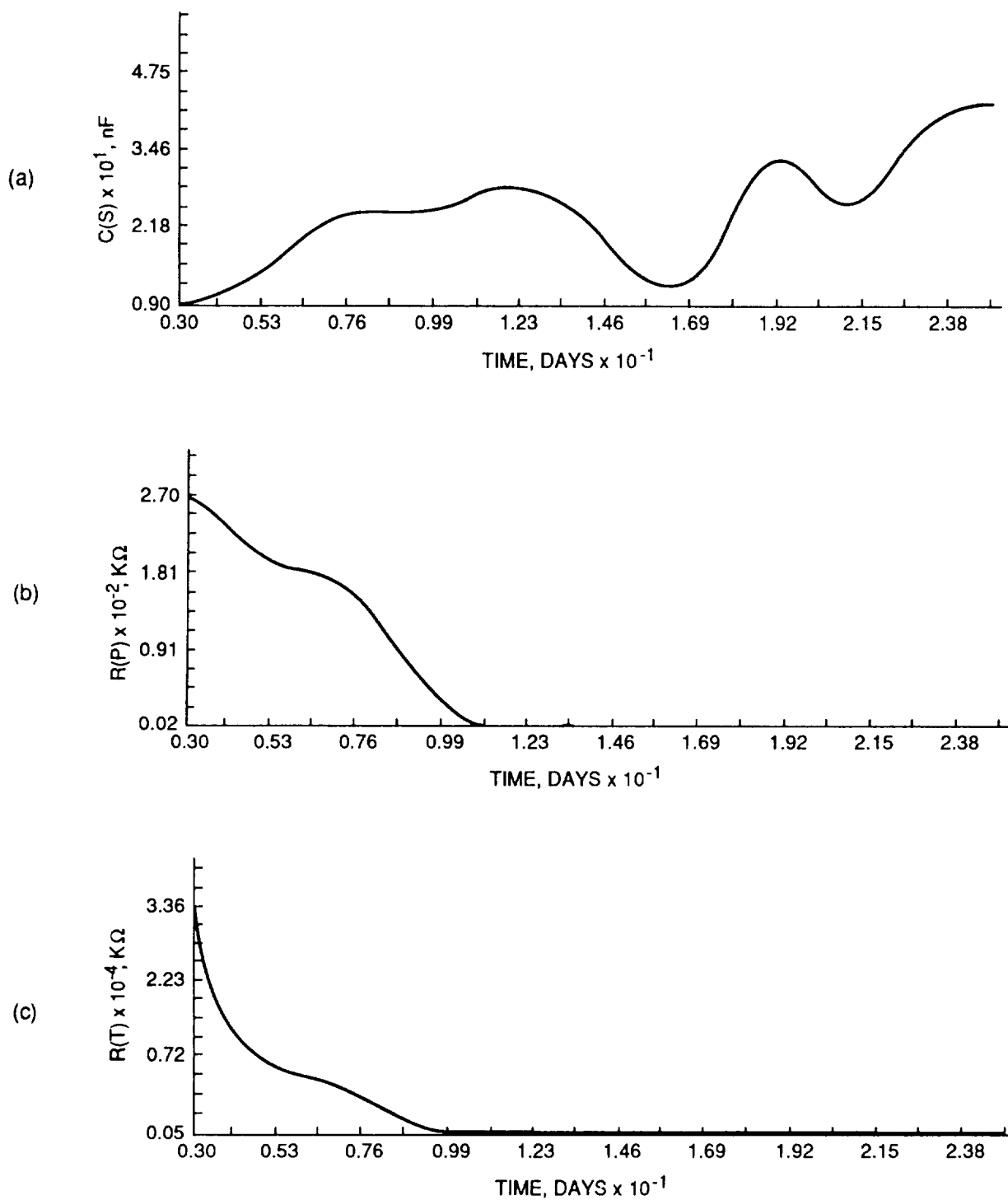
DICHROMATE SEALED
pH 9.5

(a)

(b)

(c)

Figure 20. C(S)-, R(P)-, and R(T)-time curves for dichromate seal at pH 9.5.

DICHROMATE SEALED
pH 9.5

(a)

(b)

(c)

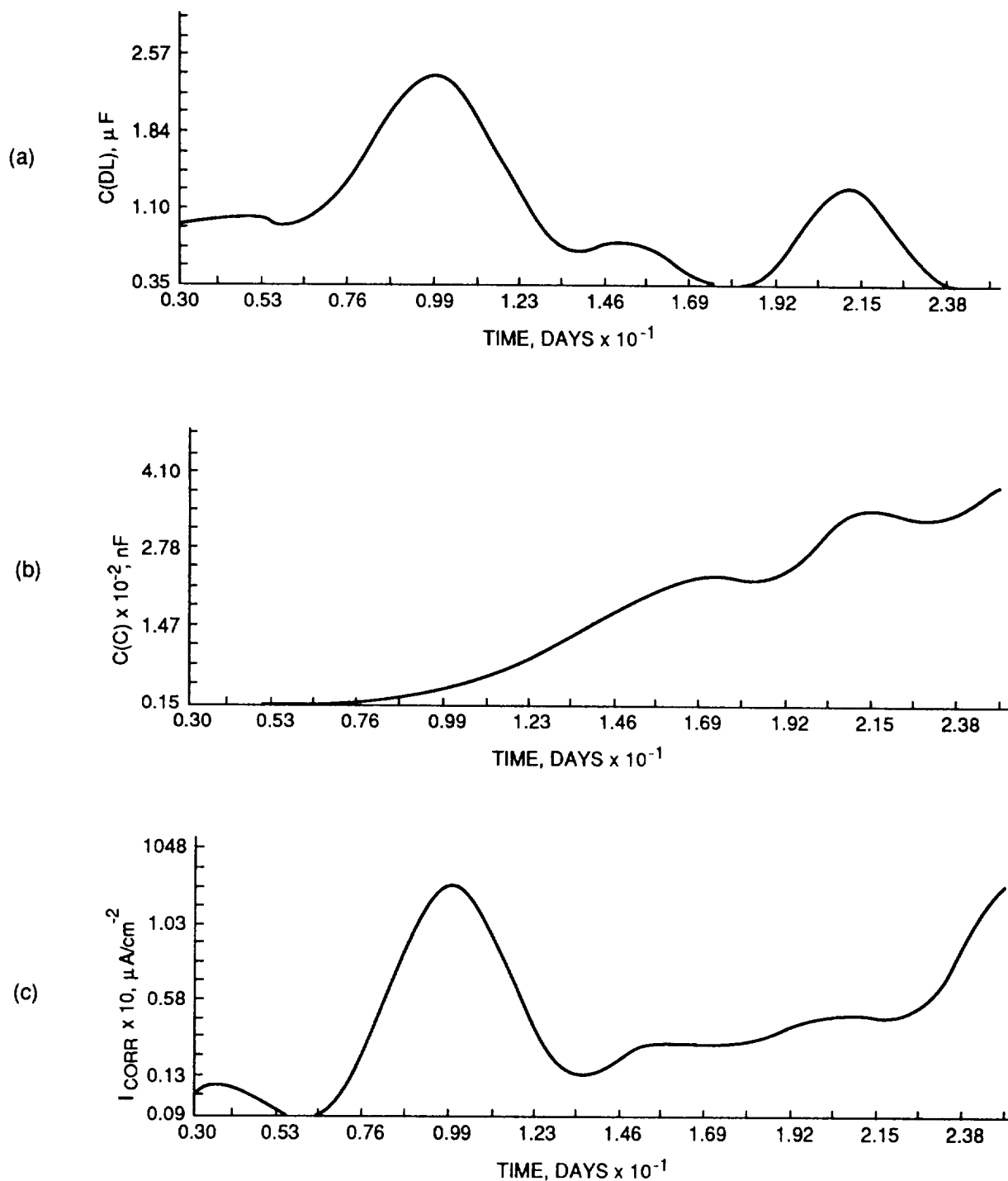
Figure 21. C(DL)-, C(C)-, and I_{CORR}-time curves for dichromate seal at pH 9.5.

Table 1. Average values of corrosion rates

Material 6061-T6 Al	Seal	Thickness Microns	pH	Average Corrosion Rate, First 7 Days, Mils/year	Average Corrosion Rate, 28 Days, Mils/year
Bare Aluminum*	—	—	9.5	0.75	—
			5.2	1.91	
Hard Anodized Aluminum	$CR_2O_7^{-2}$	45.7	9.5	0.00113	0.0032
			5.2	0.00020	0.0058
Anodized Aluminum	Polyurethane	10.2	9.5	0.0319	0.0545
			5.2	0.00026	0.0398
Anodized Aluminum	$Cr_2O_7^{-2}$	10.2	9.5	0.00031	0.0196
			5.2	0.00003	0.0577

*Corrosion rate measured on first day only.

Table 2. Composition of 6061-T6 aluminum

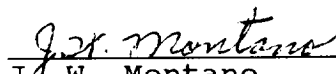| Element	Listed Weight Percent (The Aluminum Association, Inc.)	Observed Weight Percent (MSFC Analysis)
Cu	0.15–0.40	0.36
Mg	0.8–1.2	1.01
Ti	0.15 max	0.01
Fe	0.7 max	0.50
Si	0.4–0.8	0.62
Mn	0.15 max	0.04
Zn	0.25 max	0.13
Ni	0.05 max	0.02
Cr	0.04–0.35	0.17
Al	Balance	Balance

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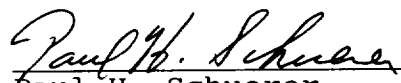
APPROVAL

THE CORROSION PROTECTION OF 6061-T6 ALUMINUM BY A POLYURETHANE-SEALED ANODIZED COAT

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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