NASA Technical Paper 3545

# The Corrosion Protection of AISI™ 1010 Steel by Organic and Inorganic Zinc-Rich Primers

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*Marshall Space Flight Center • MSFC, Alabama*

National Aeronautics and Space Administration
Marshall Space Flight Center • MSFC, Alabama 35812

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## TABLE OF CONTENTS


| | Page |
|---|---|
| INTRODUCTION | 1 |
| EXPERIMENTAL PROCEDURE | 1 |
| RESULTS AND DISCUSSION | 3 |
| Organic Primer | 3 |
| Inorganic Primer | 3 |
| Galvanic Current Measurements | 3 |
| Application to SRM/SRB | 4 |
| CONCLUSIONS/RECOMMENDATIONS | 4 |
| REFERENCES | 6 |

## LIST OF ILLUSTRATIONS


| Figure | Title | Page |
|---|---|---|
| 1. | Equivalent circuit model used for analysis of EIS data | 7 |
| 2. | Charge transfer resistance, organic primer | 8 |
| 3. | Pore resistance, organic primer | 8 |
| 4. | $I_{CORR}$, organic primer | 9 |
| 5. | Coating capacitance, organic primer | 9 |
| 6. | Charge transfer capacitance, organic primer | 10 |
| 7. | Charge transfer resistance, inorganic primer | 10 |
| 8. | Pore resistance, inorganic primer | 11 |
| 9. | $I_{CORR}$, inorganic primer | 11 |
| 10. | Coating capacitance, inorganic primer | 12 |
| 11. | Charge transfer capacitance, inorganic primer | 12 |
| 12. | Comparison of $I_{CORR}$ curves for organic and inorganic primers | 13 |
| 13. | Comparison of pore resistances for organic and inorganic primers | 13 |

TECHNICAL PAPER

# THE CORROSION PROTECTION OF AISI™ 1010 STEEL BY ORGANIC AND INORGANIC ZINC-RICH PRIMERS

## INTRODUCTION

The Space Transportation System (STS) solid rocket boosters (SRB's) consist of reusable solid rocket motors (SRM's) that provide the major source of thrust during the first 2 min of launch. After separation and parachute deployment, the motors splash down in the Atlantic Ocean and are recovered. Recovery and towback operations usually take 24 to 36 h. During this period, the aggressive seawater environment causes severe corrosion of exposed bare metal hardware.

Steel components on the SRB's include the motor cases and certain components of the nozzle that are made of forged D6AC steel and the external tank attach (ETA) ring and kick ring made from 4130 steel. These components are protected from seacoast atmospheric and seawater immersion corrosion by the application of an organic protection system consisting of a zinc-rich epoxy primer and an epoxy topcoat, manufactured by Rust-Oleum™. This system has provided adequate performance for this application since inception of the shuttle program.

Pending environmental legislation, however, threatens the continued use of this primer/topcoat system. The volatile organic content (VOC) of the Rust-Oleum™ primer and topcoat is 470 and 535 gm/L, respectively. Legislation that implements the provisions of the 1990 Clean Air Act (CAA) for the aerospace industry is contained in the National Emissions Standard for Hazardous Air Pollutants (NESHAP). A specific NESHAP for the aerospace industry sets limits of 350 and 420 g/L for primers and topcoats, respectively. Without special exemption, the use of coating systems exceeding these limits will require emission control. The cost of emission control provides the primary impetus for replacement of the Rust-Oleum™ system.

Candidates for replacement of the current coating system have not been thoroughly identified, screened, and tested for applicability to SRB requirements. However, one class of coating system stands out as the most likely alternative; inorganic zinc-rich primer and inorganic topcoat. These systems have been extensively tested for their ability to protect structural steel in the Kennedy Space Center (KSC) seacoast environment and have been found to provide outstanding service. Inorganic systems are available with compliant VOC levels. Some systems contain zero VOC.

In this work, the current Rust-Oleum™ organic zinc-rich primer is compared to an inorganic zinc-rich primer formulated by AMERON™ for its efficacy in protecting steel in adverse environments. Unhardened AISI™ 1010 steel was chosen for this study because it was readily available and is highly corrosive. A study of properly hardened D6AC steel, the material comprising the booster casings, will be undertaken at a later time.

## EXPERIMENTAL PROCEDURE

Flat plates, 10.2 by 15.2 cm (4 by 6 in), of AISI™ 1010 steel were coated with zinc-rich primer, one with the organic type manufactured by the Rust-Oleum™ Corporation and the other with an inorganic type manufactured by the Ameron™ Company. Before coating, the plates were grit blasted

and cleaned with alcohol and acetone. Each of the primer-coated plates were clamped into flat corrosion cells manufactured by EG&G-PARC and exposed to a 3.5-percent solution of sodium chloride (Na-Cl). Corrosion data were obtained over a period of 21 days, with silver/silver chloride reference electrodes being used in both cases.

Both the alternate current (ac) electrochemical impedance spectroscopy (EIS) and the direct current (dc) polarization resistance (PR) techniques were employed in this investigation. Both the EIS and the PR methods were used for study of the inorganic primer. However, the organic primer was not amenable to study by the PR method due to the low corrosion currents generated and only EIS was used in that case.

The EG&G-PARC model 378 impedance system was used for the collection of EIS data. 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 (FFT) 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 by a computer using the autoexecute procedure, with all data merged to a single set for each run. These data were subsequently processed and analyzed using the model shown in figure 1. The same computer was used to continue the experiment.

Data for the PR technique were collected using the same type of instrumentation with the EG&G-PARC model 352 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.

For the EIS data, values for each of the circuit components in figure 1 were treated as parameters in the nonlinear ORGLS[1] least-squares program, 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). Corrosion currents and, hence, corrosion rates were obtained using the PR technique for the inorganic primer. Estimates of the corrosion currents for the organic primer were obtained from EIS data using the Stern-Geary[2–4] equation for charge transfer control using estimated Tafel constants (50 mV each for $b_a$ and $b_c$) and $(R_t+R_f)$ as the total charge transfer resistance:

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

Experience has shown that the Tafel constants obtained by the PR method are usually in the neighborhood of 50 mV.

In the PR method used for the inorganic primer, curves of potential versus current were obtained and the data were analyzed using the program POLCURR.[5] The theory for the PR technique has been described previously.[2–4] All corrosion currents obtained in this work are believed to be largely due to the corrosion of zinc. Values for the corrosion rates in mils/year (mpy) may be obtained by the relation:

$$\text{Corrosion Rate (mpy)} = \frac{0.1288\, E\, I_{CORR}}{d} \quad . \tag{2}$$

In equation (2), $E$ is the equivalent weight of the corroding metal in grams, $I_{CORR}$ is the corrosion current density ($\mu$A/cm$^2$), and $d$ is the density of the metal.

## RESULTS AND DISCUSSION

### Organic Primer

The charge transfer resistance ($R_t$)-time curve for this primer is shown in figure 2, and it shows that this parameter is increasing in value with time. The pore resistance ($R_p$)-time curve is shown in figure 3 and decreases with time. The corrosion current ($I_{CORR}$)-time curve, with values estimated from EIS measurements, is shown in figure 4, and it indicates that this parameter generally decreases with time. The coating capacitance ($C_c$)-time curve is shown in figure 5, and the charge transfer capacitance ($C_{dl}$)-time curve is shown in figure 6. The $C_c$-time curve in figure 5 is oscillatory in nature, but is showing a sharp rise at the end, while the $C_{dl}$-time curve rises with time.

The rising value of $R_t$ and also of $C_c$ are compensatory in nature as far as contribution to the total impedance is concerned. However, the average value of the charge transfer resistance $R_t$ is 38.1 kohms, which is quite high. The declining value of the $R_p$-time curve in figure 3 contributes to a lower overall impedance, a trend usually observed in coated metal systems. This indicates that the pores in the primer are not being filled to a great extent. The average value of $R_p$ is 1.57 kohms, a rather high value. The average value of $I_{CORR}$ was 0.303 $\mu A/cm^2$, a rather low value considering that zinc is the most likely source of metal corrosion. The declining value of $I_{CORR}$ in figure 4 is contrary to the trend usually observed for coated metal systems, and indicates that the corrosion protection afforded the steel by zinc gradually decreases with time.

### Inorganic Primer

The $R_t$-time curve, shown in figure 7, rises with time. The average value of $R_t$ in this case is 0.27 kohms, a very low value, although the trend is the same as that for the organic primer. The $R_p$-time curve is shown in figure 8, showing a steadily rising trend. This trend is contrary to that observed for the organic primer, with the average value being only 0.094 kohms. This value is very low compared with an average value of 1.57 kohms for the organic primer. This low value indicates that the porosity is very high. The $I_{CORR}$ values obtained from PR measurements decrease rapidly with time during the first 5 days and decrease slowly thereafter (fig. 9). The average value was 9.0 $\mu A/cm^2$, very much higher than that for the organic primer (0.303 $\mu A/cm^2$). Diffusion of the medium had occurred to a radius of about 5 cm (2 in) from the point of exposure, which consisted of a total area of only 1 $cm^2$. Thus, it is likely that the corrosion current arose from an area much larger than the exposed area, verifying that diffusion was indeed rampant. In general, the very high-average value of $I_{CORR}$ points to much better corrosion protection of the steel by the inorganic primer than that for the organic primer. The coating capacitance, $C_c$, was quite large at the beginning (63,999 kohms), but dropped rapidly after 5 days. The $C_c$ curve for the period 5 to 21 days is shown in figure 10. The $C_{dl}$-time curve is shown in figure 11, showing a gradually increasing trend, similar to that for the organic primer. The values for this curve were also comparable to those for the organic primer. Figures 12 and 13 show comparison of the $I_{CORR}$-time and $R_p$-time curves, respectively, for the organic and inorganic primers.

### Galvanic Current Measurements

Galvanic current measurements were made with a flat cell especially designed for such purposes by EG&G-PARC. AISI™ 1010 steel plates coated with each type of primer were clamped into one end of the cell, with a bare, grit-blasted steel plate clamped into the other end. The areas exposed to the

medium were 1 $cm^2$ for both plates. Current measurements were made individually on each primer coated plate, using the EG&G-PARC model 352 software, over a 24-h period. The mean galvanic current for each primer was calculated. The mean current for the plated coated with organic primer was 38.8 $\mu A/cm^2$, while that for a plate coated with inorganic primer was 135.2 $\mu A/cm^2$. Both currents were relatively large because of the zinc-rich primers that were acting as the anode. The potentials displayed by both primers were close to that reported for pure zinc; namely, 1,050 mV (SCE),[6] although the values are somewhat more positive for the organic primer. The very high value of the galvanic current observed in the case of the inorganic primer indicates a very high degree of cathodic protection for the steel, although diffusion of the medium may have played a role in the high current observed. At the end of the 24-h test, there was no sign of corrosion on the bare steel plate for either primer.

### Application to SRM/SRB

Applicability of this work to the SRM/SRB lies in the need to replace the current zinc-rich primer/epoxy topcoat system due to environmental considerations. Since the current primer has a good 20-year service record, the best candidate replacements would be materials of similar composition which are environmentally compliant. The AMERON™ coating tested here fits both of these criteria. However, the AMERON™ coating is only one of several inorganic zinc-rich primers which have demonstrated outstanding performance in the KSC seacoast environment,[7] so that more than one system may be qualified, eliminating sole source problems.

One restriction to the applicability of the inorganic zinc-rich primer to SRM hardware lies in areas of high tensile residual stress, such as the SRM stiffener stubs. Compressive yielding in these areas at splashdown results in extremely high residual tensile stresses. In addition, yielding usually results in damage to the paint system, exposing both bare steel and zinc-rich primer. The zinc-rich primer has been implicated as a contributor to stress corrosion cracking in these areas. The mechanism of cracking assisted by the primer involves high tensile stress, seawater immersion, and exposed steel and primer. Preferential corrosion of the primer generates hydrogen that may be absorbed by the adjacent steel at an electrochemical potential that is cathodic to the steel corrosion potential. Since the inorganic primer provides a substantially higher corrosion current, it is expected that this effect would be intensified, producing more hydrogen and, hence, increasing the probability of hydrogen assisted cracking and crack growth. Therefore, inorganic zinc-rich primers should not be used in areas of high tensile stress. Investigation of alternate primers for motor stiffener stubs should be a separate study, concentrating on corrosion inhibiting primers rather than cathodic protection primers, since inhibiting primers will not generate hydrogen and may still be able to protect the bare metal exposed after splashdown.

## CONCLUSIONS/RECOMMENDATIONS

This work has demonstrated the superiority of the inorganic zinc-rich primer in protecting steel. Electrochemical galvanic corrosion testing of the zinc-rich primers coupled to AISI™ 1010 steel showed that the galvanic current generated with the inorganic primer as the anode exceeded that generated with the organic primer by a factor of 3.5. During the 21-day EIS/PR study, the mean corrosion current generated by the inorganic zinc-rich primer exceeded that by the organic primer by a factor of 30. This factor increases to 77 when only the first 24 h of immersion are considered, which is the time period most critical for SRB applications due to the seawater immersion experienced during towback. These results show unequivocally that the inorganic primer provides better cathodic protection.

Individual equivalent circuit parameter values taken from nonlinear least-squares fit of EIS data further confirm these conclusions. In general, a difference of two orders of magnitude was observed

when comparing like resistances in the early stages of immersion. A direct comparison of the pore resistances was made in figure 13. The low pore resistance is indicative of high porosity, leading to a greater apparent surface area for the inorganic primer.

Based on these results, it is recommended that testing to qualify a replacement for the current Rust-Oleum™ primer be initiated. Since the inorganic zinc-rich primers have been extensively tested in KSC atmosphere and retested in this report, additional corrosion testing would not be required for application to case acreage or to the ETA ring or kick ring, which are not considered to be high stress areas.

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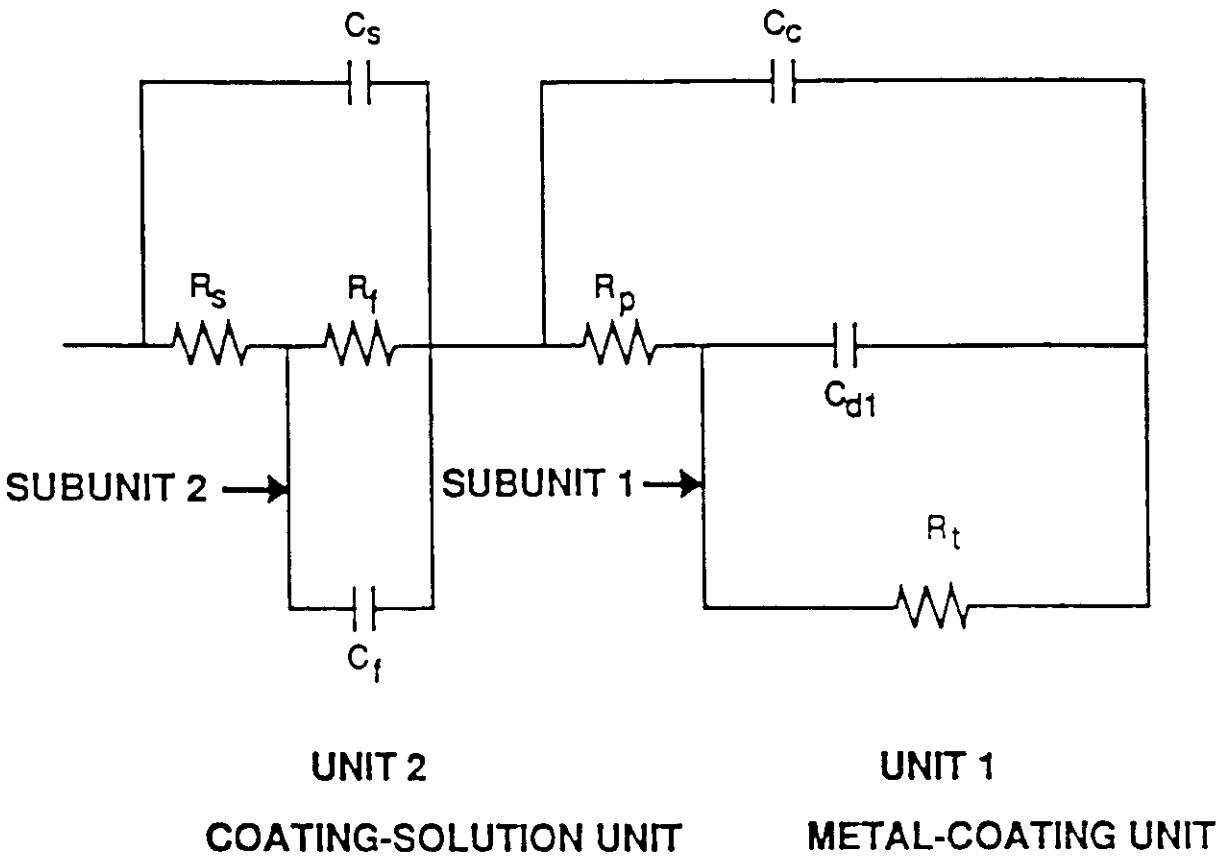


| | |
|---|---|
| $C_s$ | SOLUTION CAPACITANCE |
| $R_s$ | SOLUTION RESISTANCE |
| $C_f$ | FARADAIC CAPACITANCE (COATING/SOLUTION) |
| $R_f$ | FARADAIC RESISTANCE |
| $C_c$ | COATING CAPACITANCE |
| $R_p$ | COATING RESISTANCE |
| $R_t$ | CHARGE TRANSFER RESISTANCE |
| $C_{d1}$ | METAL/COATING INTERFACE CAPACITANCE |

Figure 1. Equivalent circuit model used for analysis of EIS data.

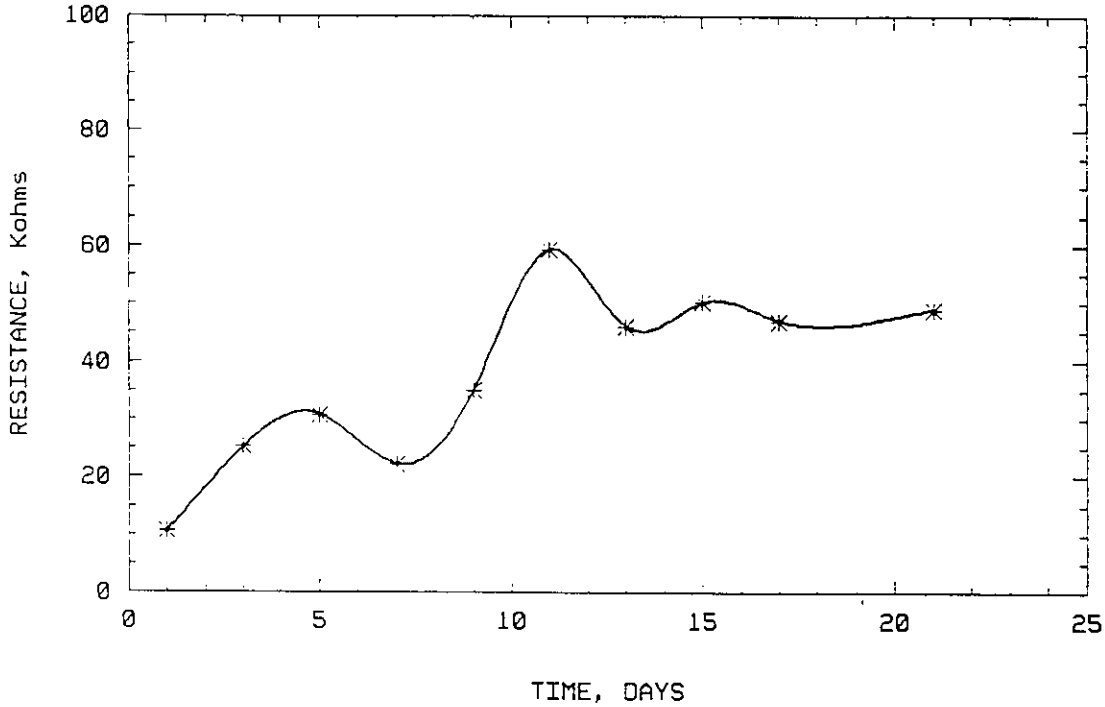


Figure 2. Charge transfer resistance, organic primer.

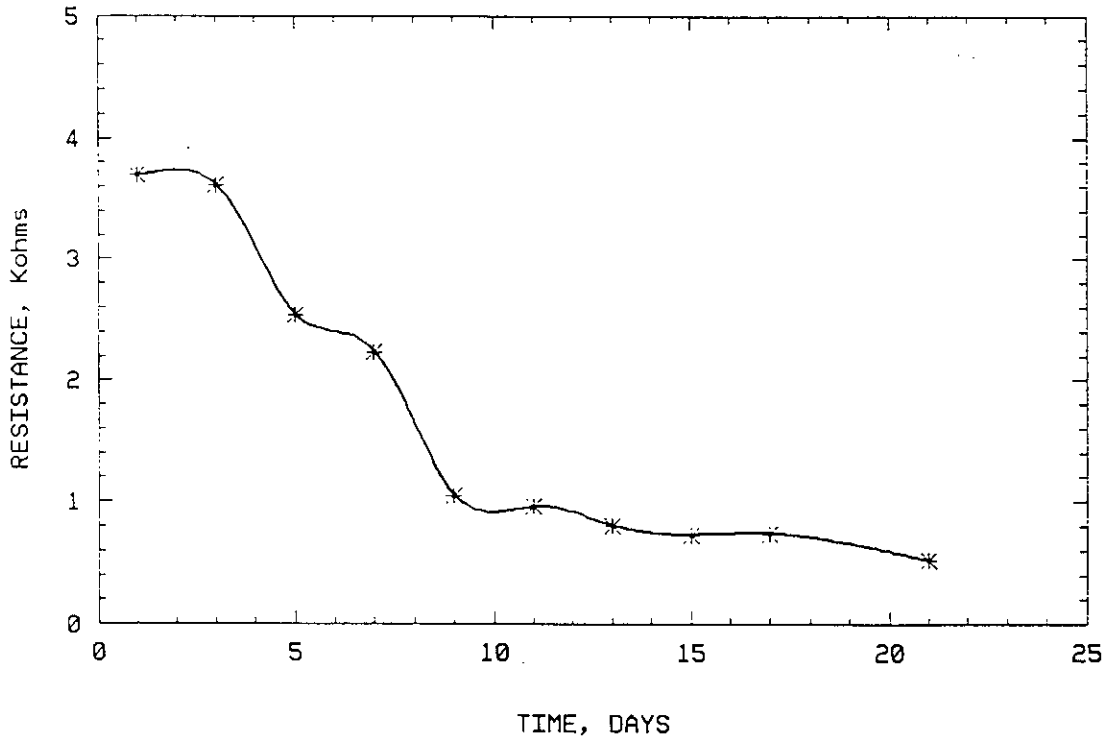


Figure 3. Pore resistance, organic primer.

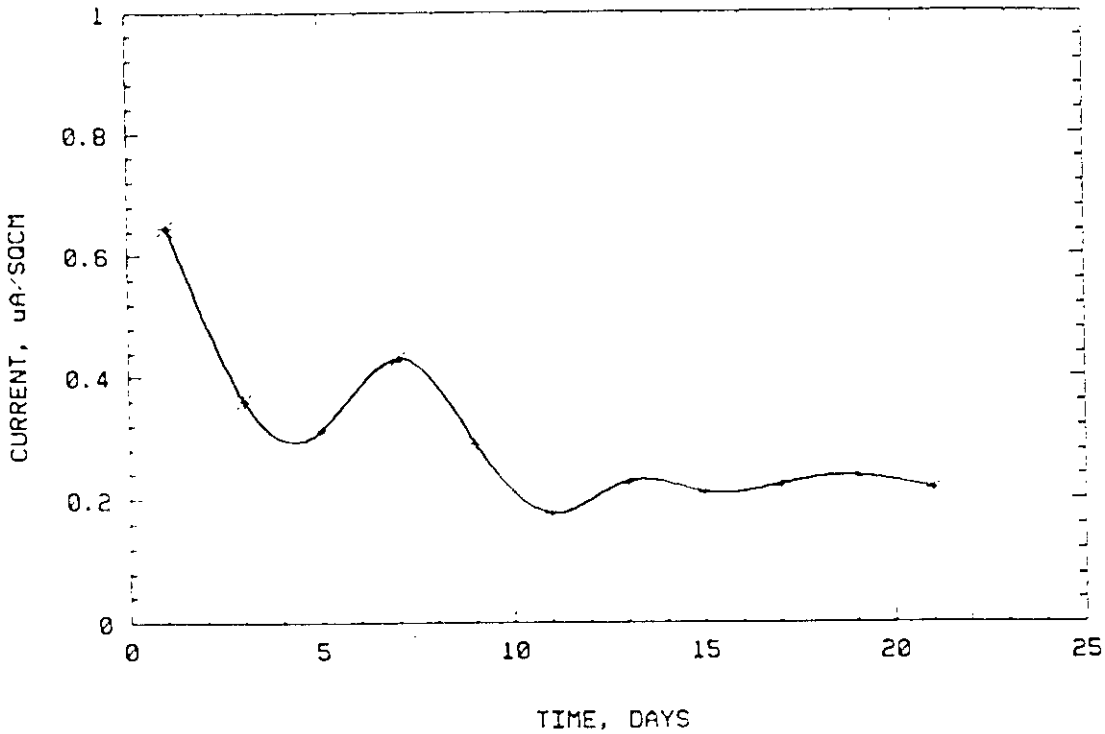


Figure 4. $I_{CORR}$, organic primer.

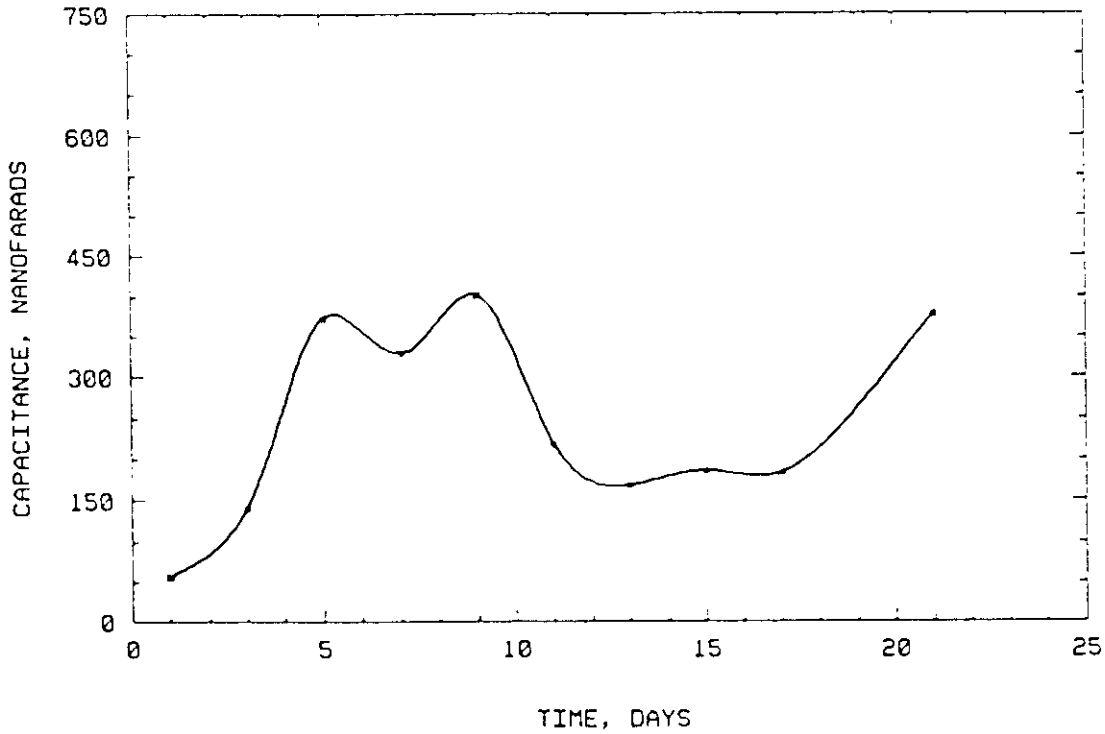


Figure 5. Coating capacitance, organic primer.

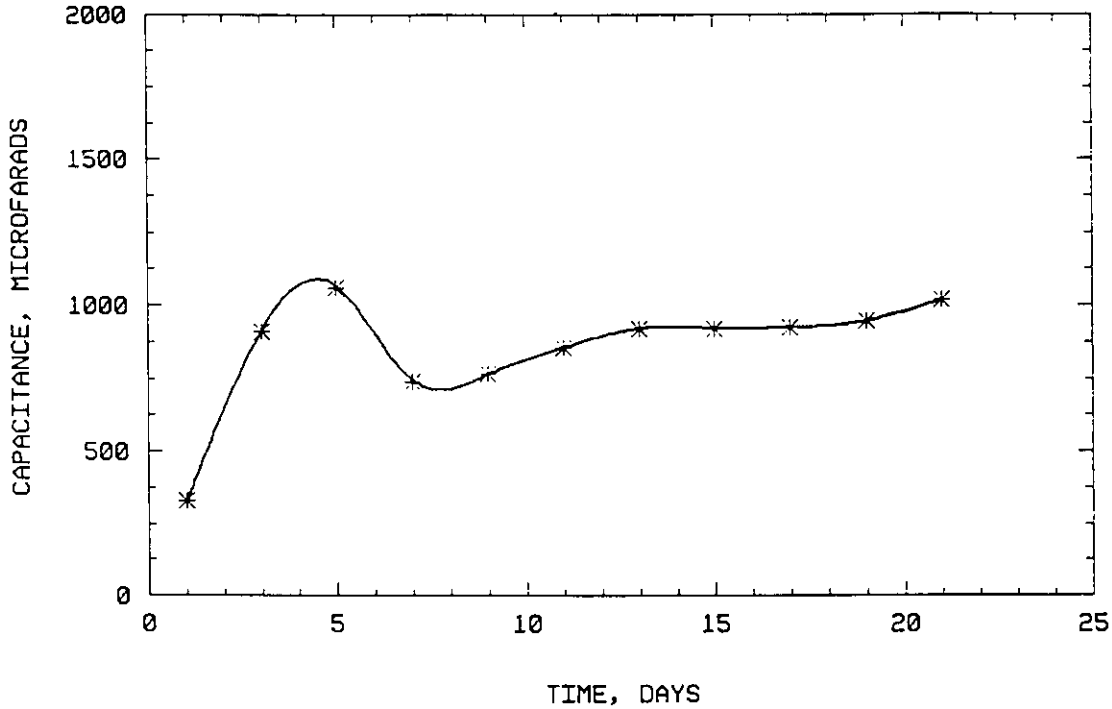


Figure 6. Charge transfer capacitance, organic primer.

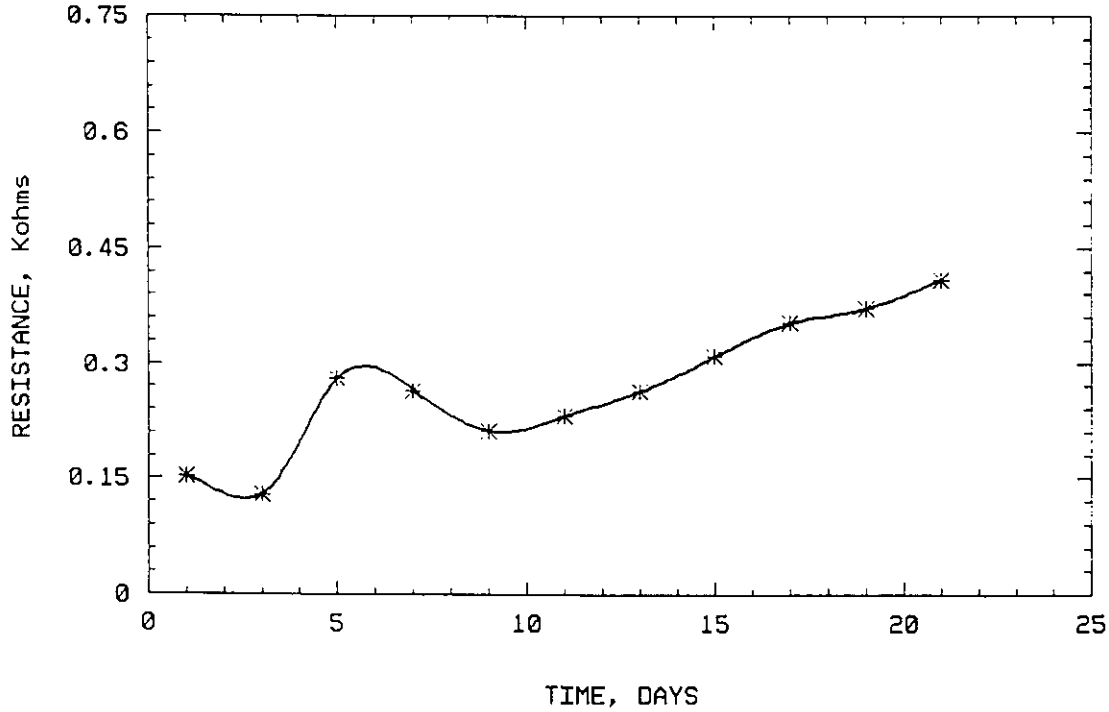


Figure 7. Charge transfer resistance, inorganic primer.

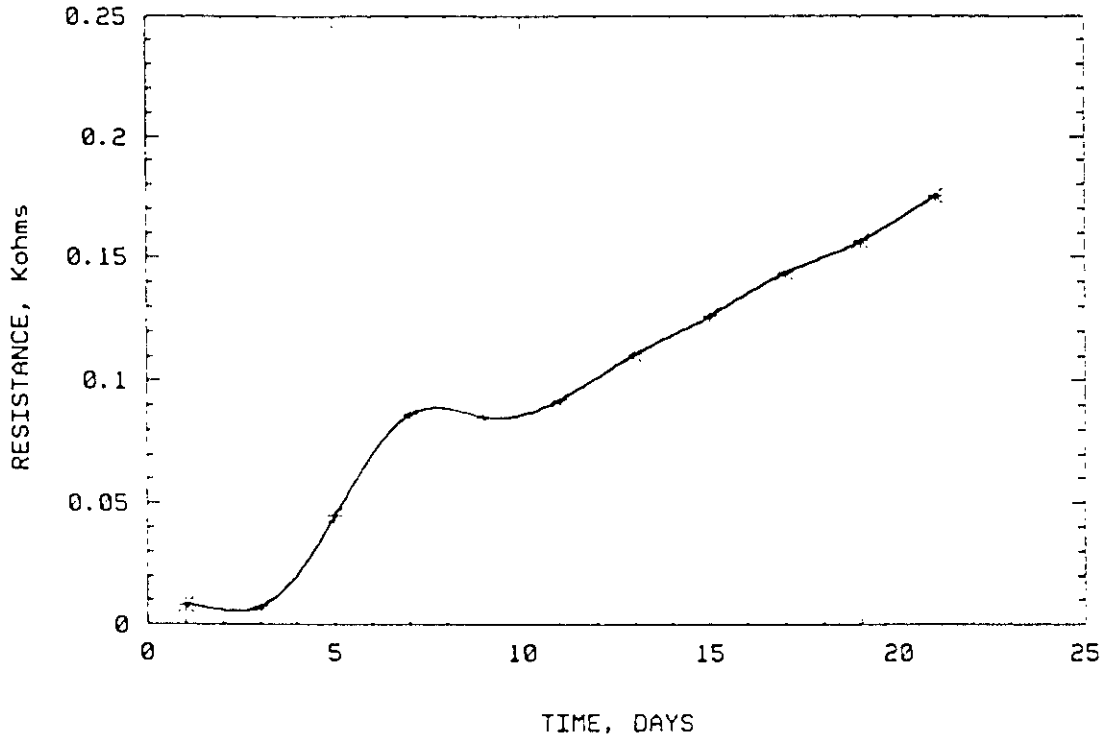


Figure 8. Pore resistance, inorganic primer.

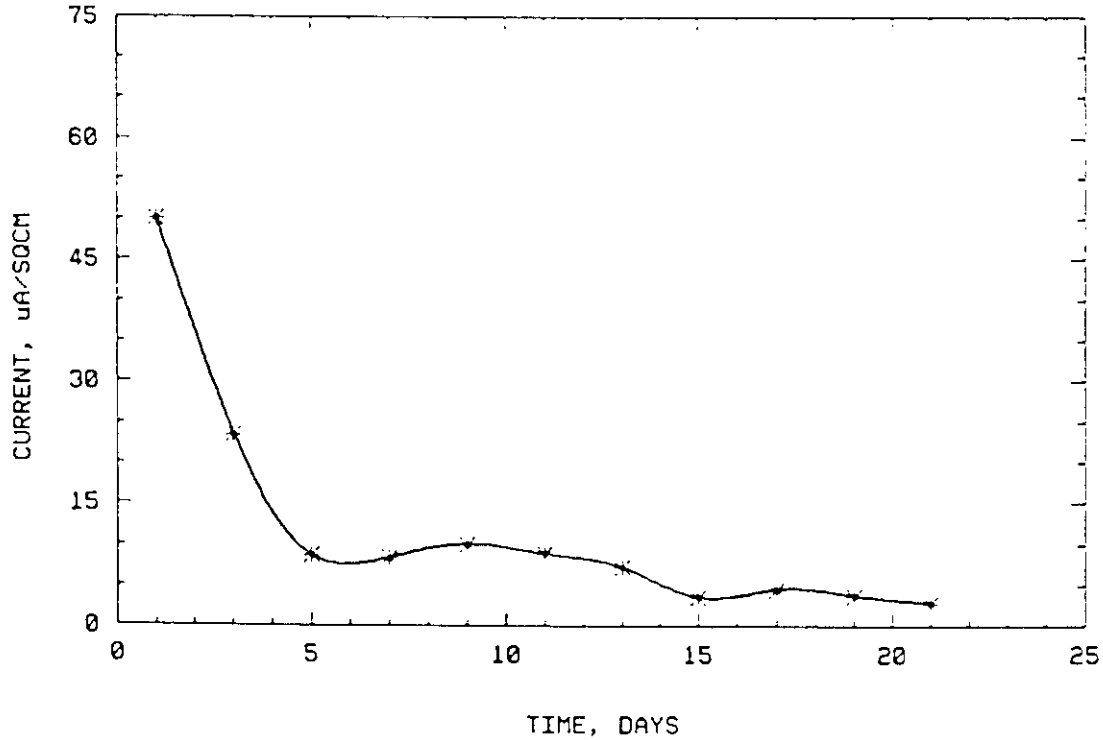


Figure 9. $I_{CORR}$, inorganic primer.

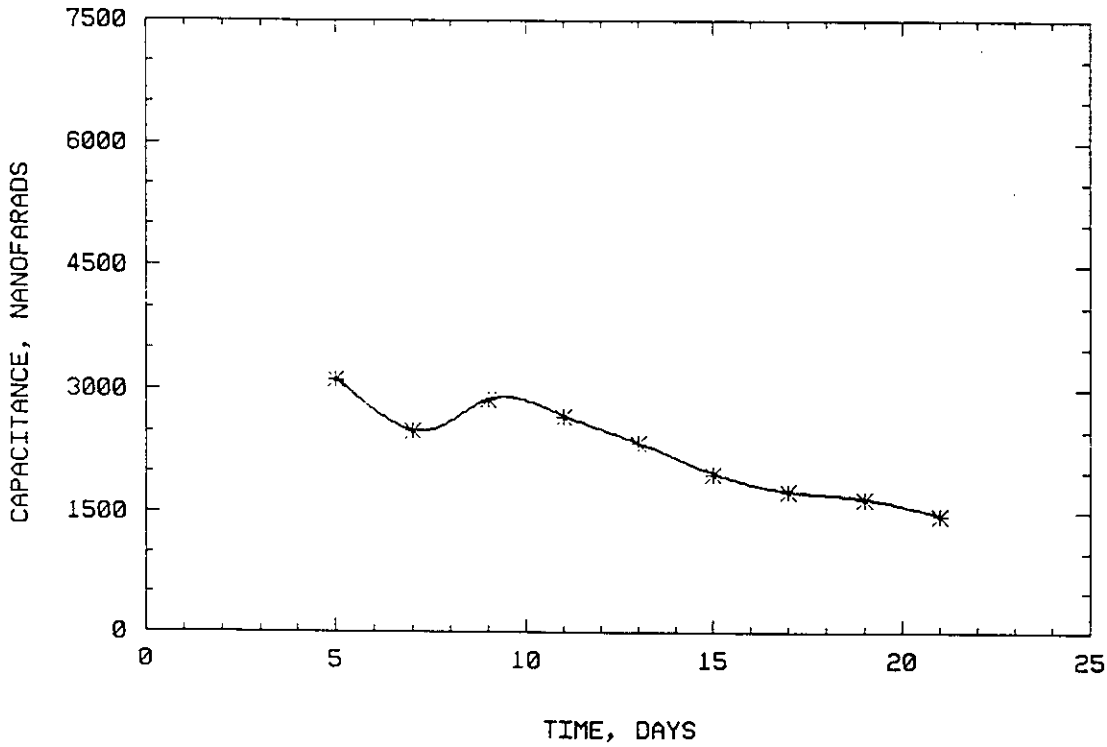


Figure 10. Coating capacitance, inorganic primer.

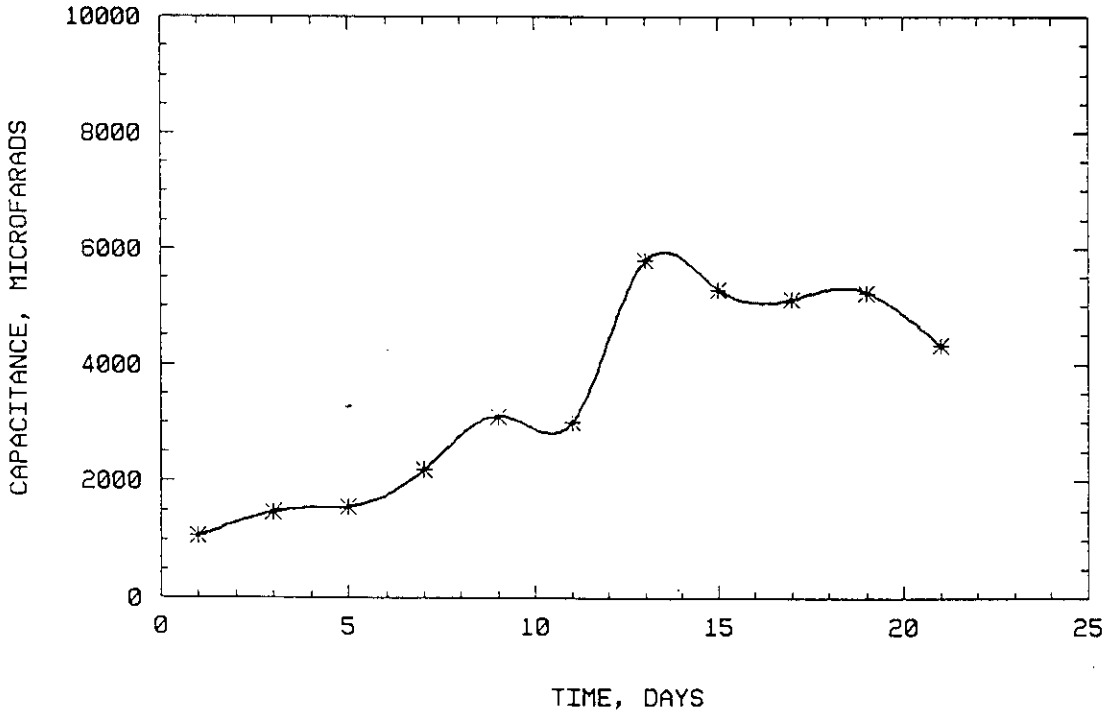


Figure 11. Charge transfer capacitance, inorganic primer.

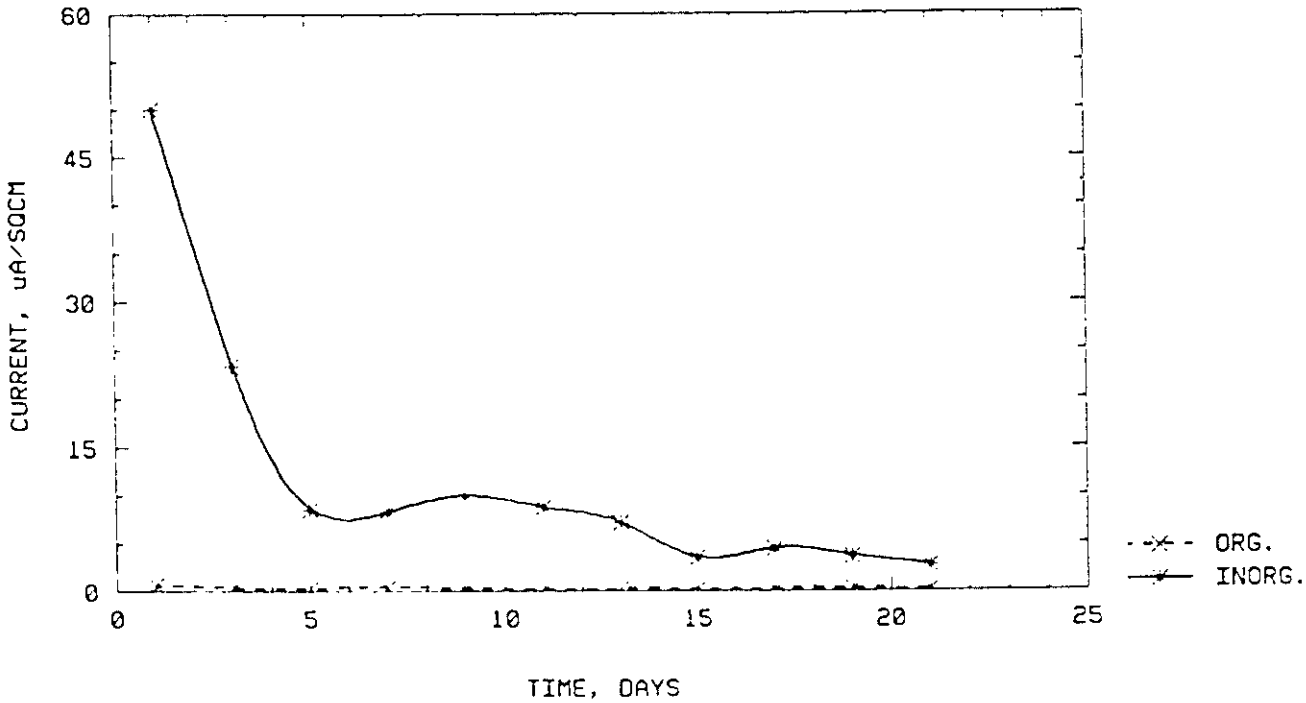


Figure 12. Comparison of $I_{CORR}$ curves for organic and inorganic primers.

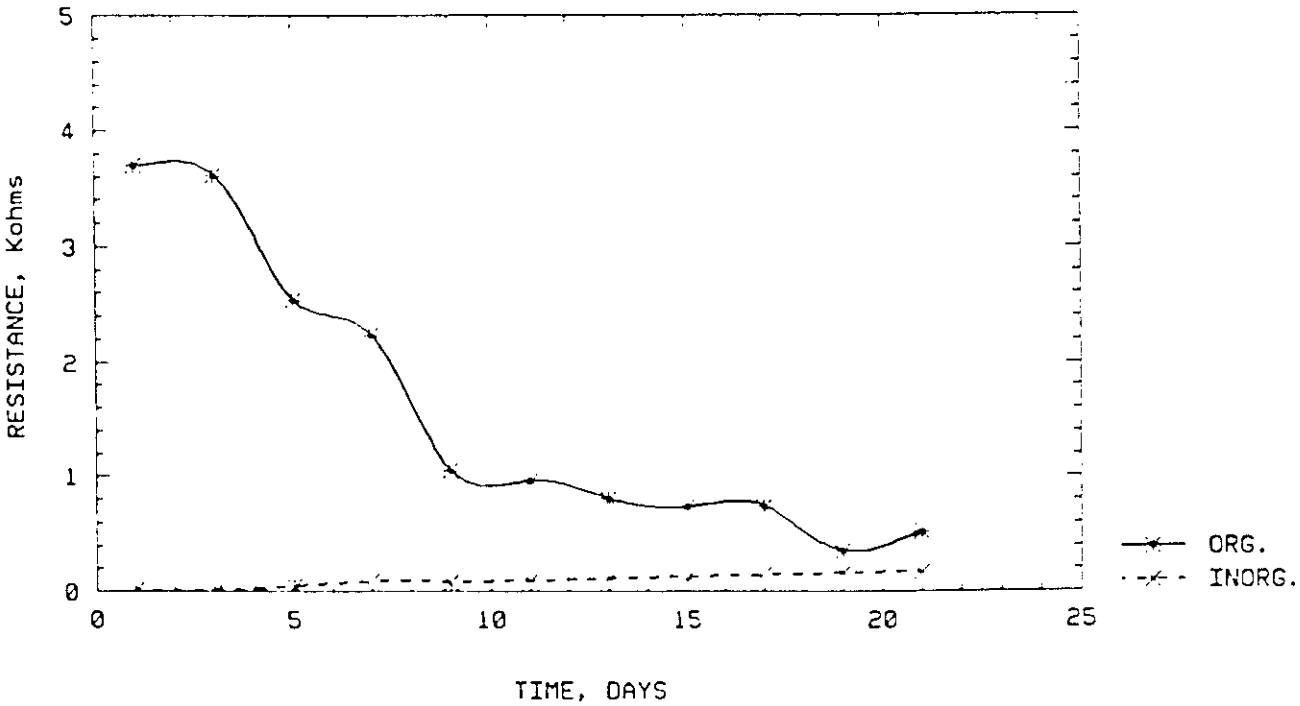


Figure 13. Comparison of pore resistances for organic and inorganic primers.

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**13. ABSTRACT** *(Maximum 200 words)*

The behavior of zinc-rich primer-coated AISI™ 1010 steel in 3.5-percent Na-Cl was investigated using electrochemical techniques. The alternating current (ac) method of electrochemical impedance spectroscopy (EIS), in the frequency range of 0.001 to 40,000 Hz, and the direct current (dc) method of polarization resistance (PR), were used to evaluate the characteristics of an organic, epoxy zinc-rich primer and an inorganic, ethyl silicate zinc-rich primer. A dc electrochemical galvanic corrosion test was also used to determine the corrosion current of each zinc-rich primer anode coupled to a 1010 steel cathode. Duration of the EIS/PR and galvanic testing was 21 days and 24 h, respectively. The galvanic test results demonstrated a very high current between the steel cathode and both zinc-rich primer anodes (38.8 and 135.2 $\mu A/cm^2$ for the organic and inorganic primers, respectively). The results of corrosion rate determinations demonstrated a much higher corrosion rate of the zinc in the inorganic primer than in the organic primer, due primarily to the higher porosity in the former. EIS equivalent circuit parameters confirmed this conclusion. Based on this investigation, the inorganic zinc-rich primer appears to provide superior galvanic protection and is recommended for additional study for application on solid rocket booster steel hardware.

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