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PROCEEDINGS

Effectiveness of Thin Film Fluoropolymers as Protective Coatings in Marine Environments

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ABSTRACT

Topside weapon systems and their associated hardware are exposed to a harsh marine environment that often includes high temperatures, periodic seawater wetdown and exposure to exhaust gases. Hence, it is necessary to employ corrosion resistant materials and protective coating systems to ensure availability and reliability of the weapon system. A recognized topside maintenance problem involves fretting corrosion associated with sliding parts. Wear surfaces are typically protected from corrosion by the application of lubricants. Although lubricants can be effective in controlling corrosion, they require frequent replacement to provide maximum protection. Candidate replacements for lubricants are a family of fluorocarbon impregnated thin film resins. The corrosion performance of several of these coatings as applied to aluminum, low alloy steel and stainless steel substrates is

described herein. Test panels were exposed to a marine atmospheric environment and a marine atmospheric environment with periodic seawater wetdown. Companion specimen panels were also exposed to constant immersion in aerated seawater and characterized using electrochemical impedance spectroscopy. The findings of this research indicated that fluoropolymer coatings provided better long-term protection than solid-film lubricants.

INTRODUCTION

Topside weapons systems are exposed to many different environments. For example, these might include some combination of marine atmospheric, seawater splash and spray, stack gases, fresh water, high temperature, oils, lubricants and various solvents. Therefore, concerted efforts are made to employ the best available corrosion protection schemes with the principal objectives of ensuring that weapon systems are available, reliable and maintainable. A recognized topside corrosion problem involves fretting corrosion associated with sliding parts on weapon systems. In many cases wear surfaces are coated with solid-film lubricants, which provide only modest corrosion protection. This class of lubricants are often high maintenance items and when neglected corrosion between sliding parts takes place.

The objective of this study was to compare the corrosion properties of several conventional solid-film lubricants, e.g., dry-film lubricants embedded in an organic matrix, with the behavior of thin-film fluoropolymer coatings. Test coupons were exposed to several marine environments and evaluated in the laboratory using electrochemical impedance spectroscopy (EIS). The EIS technique has been used successfully by others[1-7] to characterize and follow the degradation of protective coatings. Because impedance data are collected over a broad frequency range, typically 1 mHz to 65 kHz, the procedure is capable of identifying and quantifying individual factors contributing to coating failure, such as moisture uptake, coating conductance and interfacial corrosion.

EXPERIMENTAL

Test panels were prepared and supplied by the coating manufacturer. The fluoropolymer coatings were applied to a HY-80 steel, AISI 304 stainless steel and AA6061-T6. A list of test specimens is provided in Table 1. Two types of coatings were studied: (1) solid-film lubricants that conformed to weapon specification 20290 and are designated as 6255 and 6256; and (2) thin-film fluoropolymer coatings which are designated as 6108 and STF.

Panels were exposed for two years or more to 1) a marine atmosphere and 2) a marine atmosphere with periodic seawater wetdown. The atmospheric test racks face east and are located approximately twenty meters from the Atlantic Ocean in Ft. Lauderdale, FL. Specimens were secured to a fiberglass support using nonmetallic fasteners and positioned 30° to the horizontal. Specimens exposed to periodic seawater wetdown were positioned and secured to fiberglass supports in an identical manner; however, these racks are located about fifty meters from the ocean, but within ten meters of the Port Everglades shipping channel. Specimens placed on these racks were periodically sprayed with fresh seawater every hour for ten minutes. All outdoor specimens were examined visually and photographed periodically.

Companion panels were also exposed to aerated seawater and periodically evaluated using EIS. EIS measurements were made using a Solartron 1260 Gain Phase Analyzer coupled to an EG&G PARC 273A potentiostat and interfaced to a personal computer for scanning and data manipulation. A three electrode cell configuration was employed that utilized a glass clamp-on cell and included a commercial Ag/AgCl reference electrode and a graphite auxiliary electrode. The exposed surface area was approximately 24 cm^2. Impedance scans were generally run between 65 kHz and 10mHz at an applied amplitude of 20-40 mV. Specimens were removed from constant immersion in aerated seawater for periodic EIS testing and were immediately returned to this environment at the conclusion of the EIS scan. Data analysis was performed using Scribner and Associates ZFit® which incorporates a complex nonlinear least squares (CNLS) fitting routine.

A static friction test was also performed on virgin coated panels and coated panels after 310 days of constant immersion in aerated seawater. This test was conducted according to ASTM D 1894[8].

RESULTS AND DISCUSSION

Marine Atmospheric Exposure

All coated HY-80 steel panels experienced slight to extensive rust through and complete loss of coating adhesion on a few panels. The fluoropolymer coating (6108) provided protection that was equal to 6255 (solid-film) and was superior to the 6256 (solid-film) coating. A comparison between 6255 and 6256, each containing an intentional defect, is shown in Fig. 1. The 6256 coating had completely failed with uniform rust through and sizeable amounts of coating loss. Conversely, the 6255 and 6108 (not shown) panels exhibited moderate rusting in the "x" scribe and a few isolated rust through spots in areas away from the defect. A large number of small blisters were located adjacent to the "x" scribe on the 6255 panel but were not observed for 6108. 6256 panels without an initial defect experienced uniform failure and rust through, whereas only a few pin-head size rust spots were found on the 6108 and 6255 coated panels without intentional defects.

Coatings applied to the AA6061-T6 substrate performed well in marine atmospheric exposure. The STF coated panel showed no signs of underfilm attack or loss of adhesion near the "x" scribe on those panels containing intentional defects. 6255 coated panels also showed no evidence of coating adhesion loss or underfilm corrosion, however the 6155 coating contained a uniform distribution of discolored spots.

All coated AISI 304 panels experienced severe discoloration of the coating (Fig. 2). The nature of this deterioration remains unclear; however, no underfilm corrosion or coating adhesion loss was observed. Because of the nearly identical appearance of all coated stainless steel panels, it was impossible to rank the individual coatings in terms of performance.

Marine Atmospheric Exposure with Seawater Wetdown

Exposure to periodic seawater wetdown proved to be a more aggressive environment. All 6256 panels, those with and without intentional defects, exhibited complete loss of coating adhesion and the build-up of voluminous corrosion products. In comparison, 6255 exhibited the best performance with moderate pin-hole rusting on panels without an intentional defect and sizable corrosion product build-up along the "x" scribe on the panel containing the intentional defect. Two of five 6108 panels experienced severe uniform rusting, while the other panels showed moderate localized rusting.

Both 6255 and STF coatings on AA6061-T6 panels held up well to the more aggressive seawater wetdown environment. The discolored spots on the 6255 coating were in greater number and larger in size compared to those observed on panels exposed to the marine atmosphere only environment; however, the coating remained intact with no apparent loss of adhesion. Attack of the bare metal in the "x" scribe was more extensive for these panels compared to those exposed only to the marine atmosphere (Fig. 3). The STF coated panels also performed well however localized, white corrosion spots about the size of a pin-head were present on all panels. As with the 6255 coating no loss of adhesion was observed (Fig. 3).

The coated stainless panels exposed to the periodic seawater environment behaved identically to those specimens exposed only to the marine atmospheric environment (Fig. 2). This behavior was not exhibited by these same coatings on the HY-80 substrate, which suggests that the stainless steel substrate influenced the deterioration of the coatings. The nature of this interaction remains unclear at this time.

Electrochemical Impedance Spectroscopy

The impedance data was analyzed using a CNLS program. The electrical analogs are shown in Fig. 4. The impedance behavior of coated HY-80 specimens was best represented by Model A; whereas, Model B typically applied to both AA6061-T6 and AISI 304 coated specimens. The two models are similar except Model B contains a constant phase element in series with the coating pore resistance (R_{po}) which is associated with diffusion within coating pores. This diffusional impedance manifests itself as a broadening of the phase angle minimum in the Bode-angle plot at intermediate frequencies (ca. 100 Hz). Examples of the CNLS fit for each substrate type are shown in Figs. 5-7.

A summary of impedance data as a function of time for each coating system is provided in Tables 2-4.

From the impedance data (Table 2) and visual observations, the 6108 coating on HY-80 performed better than the 6255 and 6256 coatings. Although the R_{po} values are lower than those obtained for the 6255 coating, the change in coating capacitance (C_c) is less for the 6108 coating and the charge transfer resistance (R_{ct}) remains higher than values obtained for both 6255 and 6256. A sizeable number of coating blisters occurred on the 6255 coating while localized rust through of the 6256 coating was observed. Conversely, no signs of deterioration of the 6108 coating was evident. Results from EIS correlated well with the two years of field testing. The 6108 coated panels performed better in the marine atmospheric environment compared to the 6255 and 6256 coatings; however, performed slightly worse than the 6255 in the marine atmosphere with periodic seawater wetdown, but performed better than the 6256 in the latter environment.

As observed for coated HY-80 panels, the 6108 coating on the AISI 304 substrate performed better than the 6255 and 6256 coatings. Higher R_{po} values were obtained for the 6108 coated panel compared tc both 6255 and 6256 coated specimens. In addition, the R_{ct} was highei for the 6108 coating compared to the 6256 coating but was about twc times lower compared to the 6255 coating. Visual observations showec 1) no signs of deterioration of the 6108 coating, 2) the presence o several areas of localized attack on the 6256 coated specimen (a: indicated by the local build-up of rust colored corrosion products) and 3 blistering of the 6255 coating. Based on the impedance responses o these specimens, it would be predicted that the 6108 coating shoul perform better than the 6255 and 6256 coatings; however, evidenc from field testing was inconclusive.

R_{po} and R_{ct} values for the 6255 coating were higher than thos obtained for the STF coating. However, both the STF and 6255 coating performed similarly in the aerated seawater environment as indicated b the lack of coating deterioration. This slight difference in impedanc behavior may reflect the observed performance when these coate panels were exposed to the seawater wetdown environment. As note previously, some apparent localized attack of the aluminum substrat occurred through the STF coating whereas no deterioration of the 625 coating was evident.

Static Friction

Static friction tests were performed in order to determine whether exposure to a corrosive environment would degrade the coating's lubricity. It is apparent from the results summarized in Table 5 that deterioration of the coatings on HY-80 steel substrates leads to an increase in the static friction. On the other hand, the values for static friction decrease for most of the coatings on AISI 304 and AA6061, with the exception of the STF coating on AA6061-T6.

SUMMARY

o In general, the EIS data correlated well with the results from field testing and demonstrated that relatively short-term laboratory testing using EIS is capable of predicting the performance of these coatings when exposed for extended times in field environments.

o Results from both laboratory testing and field exposures indicated that the fluoropolymer coatings (6108 and STF) are better than the 6256 solid-film lubricant and equal to and sometimes better than the 6255 solid-film lubricant.

o Limited static friction tests revealed that the lubricity of coatings on AA6061-T6 and AISI 304 substrates did not deteriorate, while static friction values were higher for two of the three coatings on the HY-80 substrates.

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Table 1. Test Specimens.

Specimen ID #	Substrate	Coating System	Coating Thickness (μm)
T1	Steel	6108	12
T2	Steel	6256	<1
T3	Aluminum	STF	34
T4	Steel	6255	10
T5	Stainless	6255	13
T6	Aluminum	6255	45
T7	Stainless	6108	3
T8	Stainless	6256	<1

Table 2. Summary of EIS Data for Coated HY-80 Steel.

Specimen #	Time, d	R_{po} $\Omega \cdot cm^2$	C_c nF/cm^2	R_{ct} $\Omega \cdot cm^2$
T1	0	$6.6X10^5$	1.1	$3.1X10^7$
	54	$5.3X10^5$	3.0	$2.9X10^7$
	245	$7.5X10^4$	2.0	$2.0X10^7$
T4	0	$1.0X10^7$	0.4	$1.9X10^8$
	20	$3.8X10^5$	4.4	$7.4X10^5$
	41	$3.9X10^5$	4.6	$1.6X10^6$
	250	$2.5X10^5$	5.0	$3.5X10^6$
T2	0	$2.5X10^4$	132	$5.9X10^5$
	35	$1.8X10^4$	450	$1.3X10^5$
	116	$1.4X10^4$	350	$6.9X10^4$
	245	$5.7X10^3$	200	$1.4X10^5$

Table 3. Summary of EIS Data for Coated AISI 304 Stainless Steel.

Specimen #	Time, d	R_{po} $\Omega \cdot cm^2$	C_c nF/cm^2	R_{ct} $\Omega \cdot cm^2$
T7	0	$9.9X10^6$	2.4	$3.1X10^9$
	53	$7.9X10^5$	7.1	$6.9X10^7$
	245	$3.5X10^6$	22.0	$6.7X10^7$
T8	0	$3.2X10^5$	137	-
	11	$2.7X10^5$	296	$2.5X10^7$
	50	$6.2X10^5$	887	$8.8X10^6$
T5	0	$1.2X10^6$	0.95	$7.4X10^9$
	55	$1.9X10^6$	2.0	$1.3X10^9$
	246	$1.2X10^5$	1.1	$1.5X10^8$

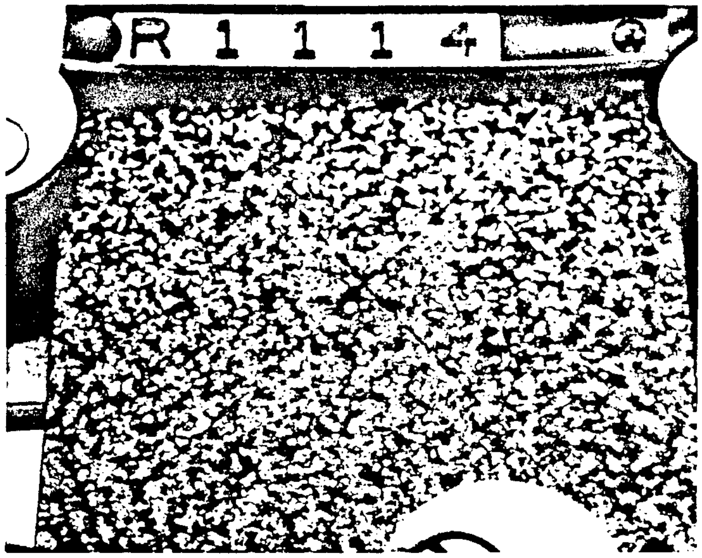
Table 4. Summary of EIS Data for Coated AA6061-T6.

Specimen #	Time, d	R_{po} $\Omega \cdot cm^2$	C_c nF/cm^2	R_{ct} $\Omega \cdot cm^2$
T3	0	$1.2X10^7$	0.7	$1.2X10^8$
	14	$4.5X10^5$	16.0	$6.7X10^7$
	36	$3.1X10^5$	5.6	$1.5X10^8$
	57	$1.8X10^5$	2.2	$9.7X10^7$
	116	$1.1X10^5$	1.2	$9.3X10^7$
	245	$1.2X10^5$	2.3	$1.7X10^7$
T6	C	$8.4X10^{10}$	0.2	-
	12	$3.6X10^5$	1.7	$1.5X10^7$
	55	$1.6X10^8$	0.7	$6.9X10^8$
	246	$7.2X10^7$	0.5	$3.3X10^8$

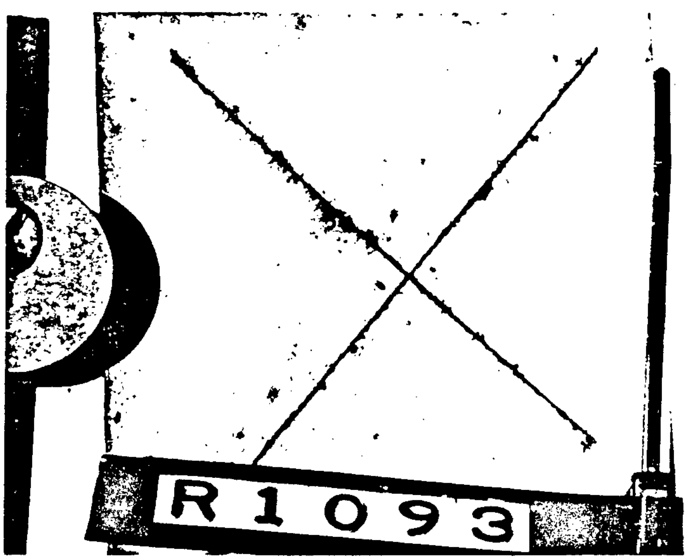
Table 5. Summary of Static Friction Test.

Specimen #	Static Friction	
	tan θ (0 d)	tan θ (310 d)
T1	.194	.271
T2	.435	.344[1]
T4	.299	.445[2]
T5	.315	.277
T7	.325	.225
T8	.325	.217
T3	.197	.249
T6	.344	.296

[1] Localized rust spots present.
[2] Large number of small diameter blisters present.

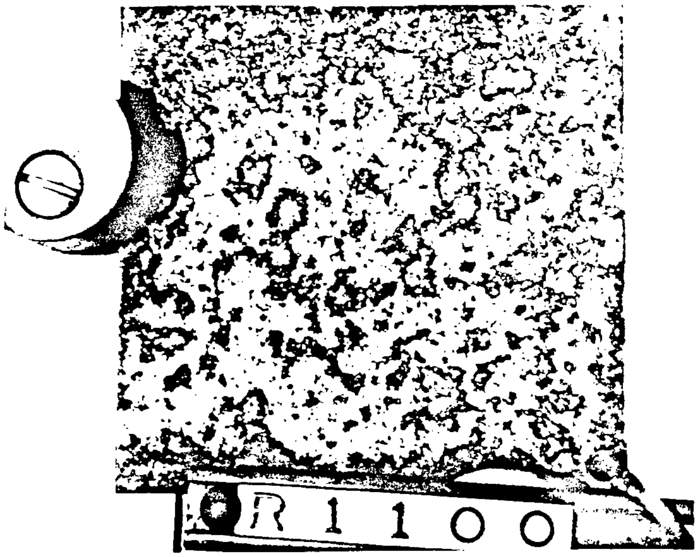


(a)



(b)

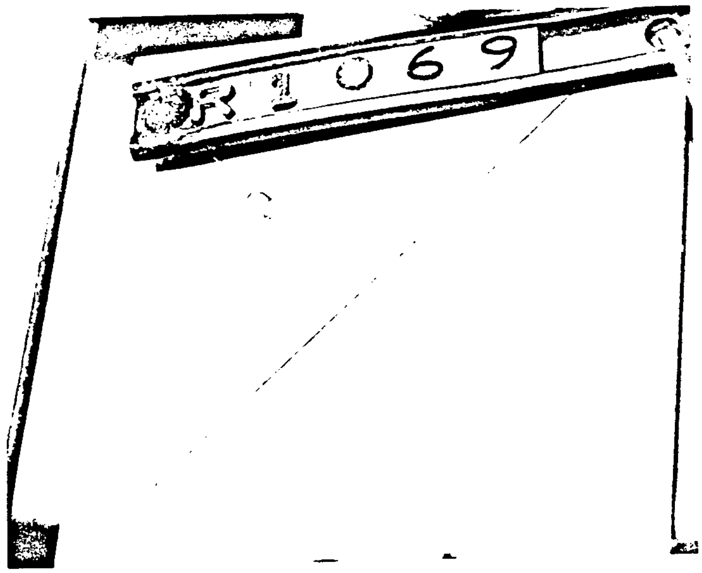
Fig. 1. Photographs of HY-80 Panels Coated with (a) 6255 and (b) 6256 after Two Years Exposure to a Marine Atmosphere.



(a)

(b)

Fig. 2. Photographs of AISI 304 Panels Coated with (a) 6255 after Two Years Exposure to a Marine Atmosphere and (b) 6108 after Two Years in Marine Atmosphere with Periodic Seawater Wetdown.



(a)

(b)

Fig. 3. Photographs of AA6061-T6 Panels Coated with (a) 6255 and (b) STF after Two Years in a Marine Atmosphere with Periodic Seawater Wetdown.

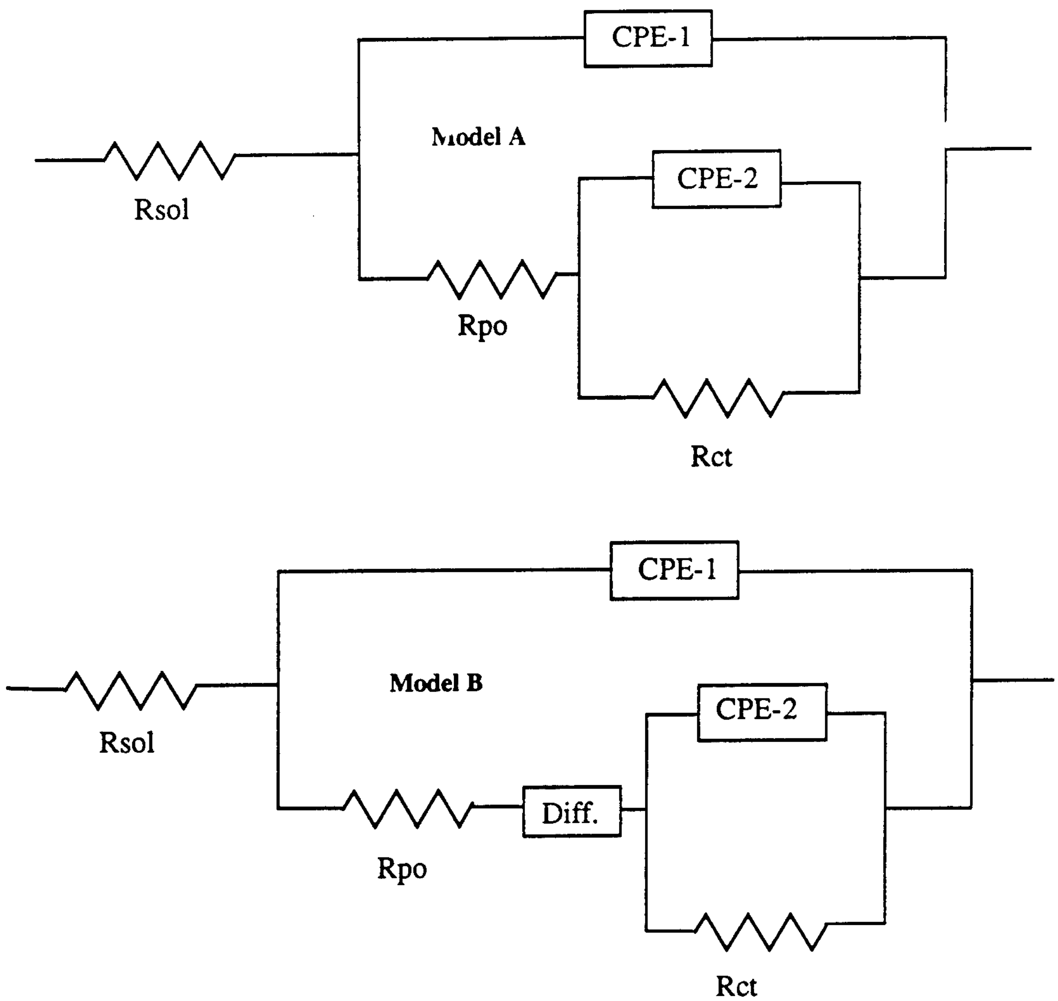


Fig. 4. Equivalent Circuit Models for (a) Coated HY-80 Steel and (b) Coated AA606-T6 and AISI 304. Rsol is the Solution Resistance, Rpo the Coating Pore Resistance, CPE-1 a Constant Phase Element that Represents the Coating Capacitance, Rct the Charge Transfer Resistance at the Coating/Metal Interface CPE-2 a Constant Phase Element that Represents the Capacitance at the Coating/Metal Interface and Diff. is aDiffusion Element (CPE-3).

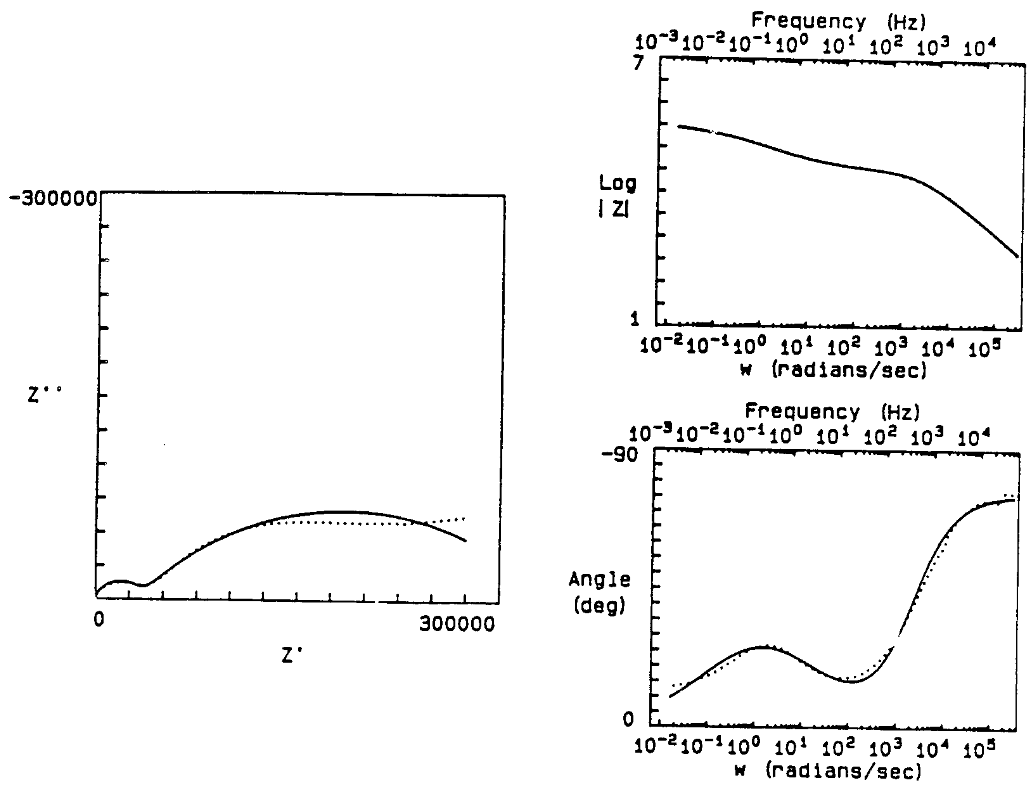


Fig. 5. Impedance plots for 6108 coated HY-80 steel immersed in aerated seawater for 120 days. Dotted lines represent experimental data and solid lines the CNLS fit (Model A).

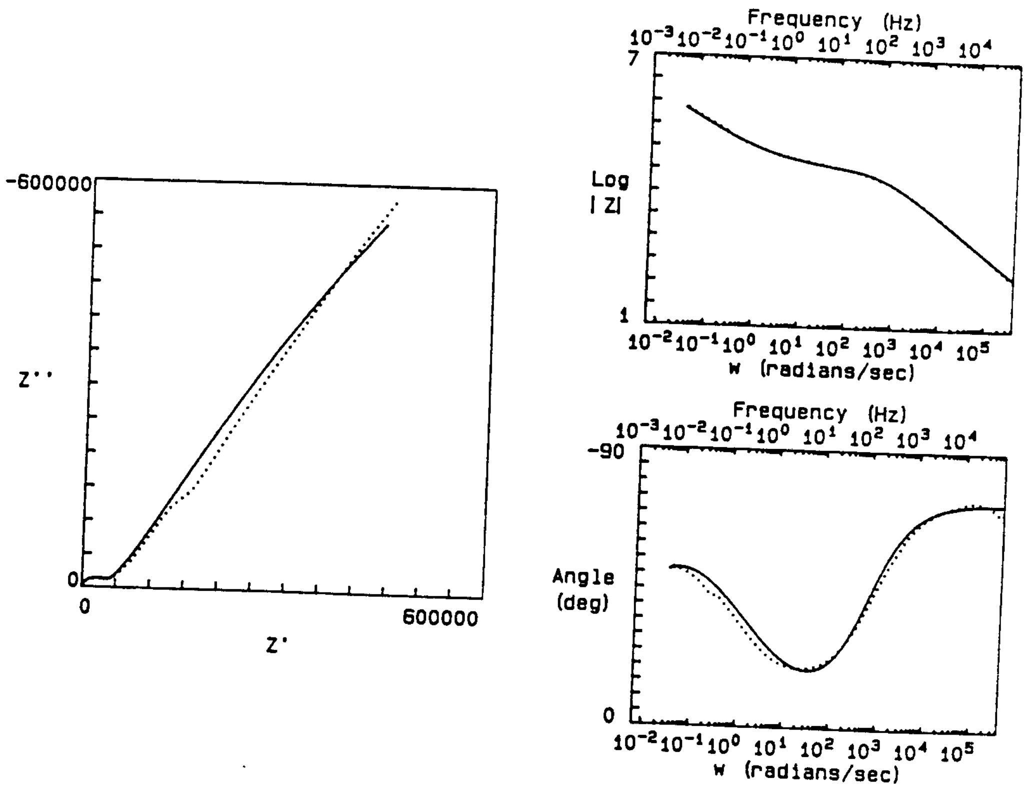


Fig. 6. Impedance plots for 6108 coated AISI 304 stainless steel immersed in aerated seawater for 53 days. Dotted lines represent experimental data and solid lines the CNLS fit (Model B).

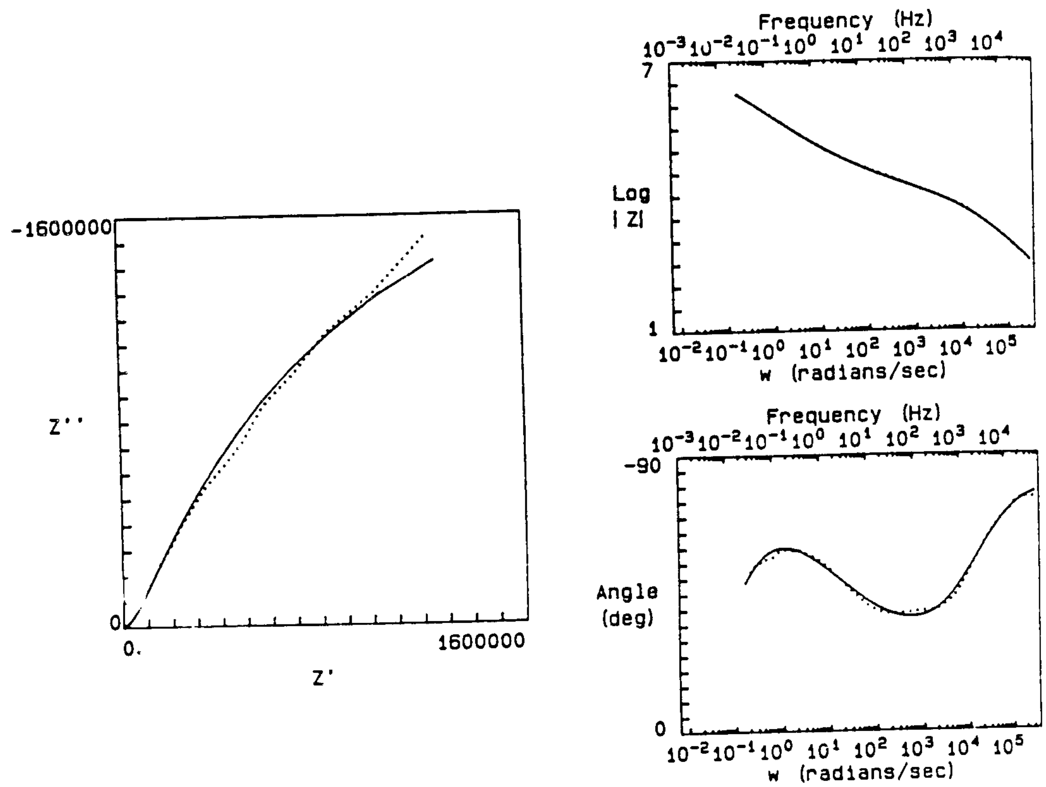


Fig. 7. Impedance plots for STF coated AA6061-T6 immersed in aerated seawater for 116 days. Dotted lines represent experimental data and solid lines the CNLS fit (Model B).