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EVALUATION OF INORGANIC ZINC-RICH PRIMERS USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) IN COMBINATION WITH ATMOSPHERIC EXPOSURE

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ABSTRACT

This investigation explored the use of Electrochemical Impedance spectroscopy (EIS) in combination with atmospheric exposure as a short term method for analyzing the performance of twenty-one commercially available zinc-rich primers. The twenty-one zinc-rich primers were: Carboline CZ-11, Ameron Devoe-Marine Catha-Coat 304, Briner V-65, Ameron D-21-9, Sherwin Williams Zinc Clad II, Carboline CZ-D7, Ameron D-4. Dupont Ganicin 347WB, Porter TQ-4374H, Inorganic Coatings IC-531, Subox Galvanox IV, Southern Coatings Chemtec 600, Glidden Glidzinc 5530, Byco SP-101, Tnemec 90E-75, Devoe Catha-Coat 302H, Glidden Glidzinc 5536, Koppers 701, Ameron D-21-5, Coronado 935-152, and Subox Galvanox V. Data were also collected on galvanized steel for comparison purposes. A library of Bode magnitude plots was generated for each coating including curves for the initial time and after each week of atmospheric exposure at the Beach Corrosion Test Site near the Space Shuttle launch pad at the Kennedy Space Center for up to four weeks. Subsequent measurements were collected after 8 weeks and after one year of atmospheric exposure. Analysis of the impedance data was performed with the purpose of identifying parameters that could be used to predict the long-term performance of zincrich primers. It has been shown that there is a correlation between the long-term performance of zinc-rich primers and several parameters obtained from EIS measurements in combination with atmospheric exposure. The equivalent circuit R₁(R₂C(R₃W)) provided a satisfactory fit for the EIS data. The corrosion potential and the R2 resistance are parameters indicative of the galvanic mechanism of protection. The capacitance of the coating is related to the barrier mechanism of protection.

SUMMARY

This investigation explored the use of Electrochemical Impedance spectroscopy (EIS) in combination with beach exposure as a short term method for analyzing the performance of twenty-one zinc-rich primers. The twenty-one zinc-rich primers were: Carboline CZ-11, Ameron Devoe-Marine Catha-Coat 304, Briner V-65, Ameron D-21-9, Sherwin Williams Zinc Clad II, Carboline CZ-D7, Ameron D-4, Dupont Ganicin 347WB, Porter TQ-4374H, Inorganic Coatings IC-531, Subox Galvanox IV, Southern Coatings Chemtec 600, Glidden Glidzinc 5530, Byco SP-101, Tnemec 90E-75, Devoe Catha-Coat 302H, Glidden Glidzinc 5536, Koppers 701, Ameron D-21-5, Coronado 935-152, and Subox Galvanox V. Data were also collected on galvanized steel for comparison purposes.

Electrochemical Measurements were performed on 10.16 cm x 15.24 cm x 0.32 cm (4-inch x 6-inch x 1/8 inch) test panels. The panel included in this investigation had been rated previously to determine their degree of corrosion performance on a scale of 1 to 10, with 10 being the highest rating. The twenty-one primers chosen represent a wide range of performance. AC impedance data were collected after one hour immersion time in 3.55% NaCl. Data were gathered in the frequency range from 100 kHz to 0.01 Hz.

A library of Bode magnitude, Nyquist, and Bode magnitude/phase angle was generated for each coating including curves for the initial time and after each week of atmospheric exposure for up to four weeks. Subsequent measurements were collected after 8 weeks and after one year of atmospheric exposure.

Analysis of the impedance data was performed with the purpose of identifying parameters that could be used to predict the long-term performance of zinc-rich primers. It has been shown that there is a correlation between the long-term performance of zinc-rich primers and several parameters obtained from EIS measurements in combination with atmospheric exposure. The equivalent circuit $R_1(R_2C(R_3W))$ provided a satisfactory fit for the EIS data. The corrosion potential and the R_2 resistance are parameters indicative of the galvanic mechanism of protection. A corrosion potential below -0.735 V Ag/AgCI [-0.780 V (SCE)] and an R_2 value that starts around 10^{-2} ohms and increases gradually with time of atmospheric exposure is indicative of good galvanic activity that results in the formation of a protective layer that has a higher resistance. The capacitance of the coating is related to the barrier mechanism of protection. Good coatings have capacitances that decrease gradually as the protective film formed by zinc corrosion products becomes less porous. This decrease in porosity is accompanied by a decrease in the water content of the film which results in lower capacitance values.

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I. INTRODUCTION

For over 25 years, the process of coating testing at the Kennedy Space Center (KSC) to identify materials for the long term protection of carbon steel structures has taken place at the Beach Corrosion Test Site near the launch pad. The atmosphere at the launch pad is highly corrosive due to the proximity of the ocean, high heat from rocket exhaust, and now with the Space Shuttle, the acidic combustion products of the Solid Rocket Boosters (SRB's). As a result of previous tests, zinc-rich primers were identified as the best choice to provide long term protection of launch structures and ground support equipment at KSC^{1,2,3}.

Exposure at the beach site provides very valuable data but it takes a long time. Testing requires 18 months for preliminary approval and continued good performance for 5 years for final approval. This investigation explores the use of Electrochemical Impedance spectroscopy (EIS) in combination with atmospheric exposure at the beach corrosion test site as a short term method for analyzing the performance of zinc-rich primers. EIS has been used before on bare metals⁴ and on zinc-rich primers⁵. The samples tested previously were flat, 0.16 cm (1/16 inch) thick coupons, 1.59 cm (5/8 inch) in diameter and did not include atmospheric exposure.

The initial stage of this investigation included EIS measurements in combination with atmospheric exposure for up to three weeks⁶. Subsequent measurements were collected after four weeks, eight weeks, and one year of atmospheric exposure.

Inorganic zinc-rich primers contain a high percentage of zinc particles (between 75% and 90%) dispersed in inorganic binders. Initially, the zinc provides cathodic protection to the steel substrate (galvanic effect). As exposure time increases, the galvanic action becomes less effective. The deposition of inhibiting zinc compounds at the base of the coating pores, followed by the sealing of the porous structure by the zinc corrosion products, results in what is referred to as the barrier mechanism of protection. The galvanic and the barrier effect must undoubtelly occur to ensure long-term protection of the steel substrate^{7,8}.

II. MATERIALS AND METHODS

A model 378 Electrochemical Impedance system manufactured by EG&G Princeton Applied Research Corporation was used for all electrochemical measurements. Electrochemical Measurements were performed on 10.16 cm x 15.24 cm x 0.32 cm (4-inch x 6-inch x 1/8 inch) test panels. Twenty-one panels were coated with the inorganic zinc-rich primers listed in Table 1. The panel rating corresponds to the degree of corrosion judged on a scale of 1 to 10, with 10 being the highest rating⁹. The 21 primers chosen represent a wide range of performance. Also listed on the table is the zinc content, and the thickness when available.

The panels were mounted on an EG&G Princeton .Applied .Research Model KO235 Flat Cell with a working electrode area of 1 cm². The flat cell (see Figure 1) consists of a flat cylinder clamped horizontally between two end plates. One end plate houses the working electrode and the other houses the platinum counter electrode. The reference silver/silver chloride electrode is housed in a Luggin well with a Luggin capillary protruding from the bottom of the well.

AC impedance data were collected after one hour immersion time in aerated 3.55% NaCl. Data were gathered in the frequency range from 100 kHz to 0.01 Hz using the Auto Execute option of the M388 electrochemical analysis software. Three experiments were performed in a sequence covering the specified frequency range and the data were automatically merged and saved. The frequency ranges for the three experiments were 100 kHz to 5 Hz, 10 Hz to 0.1 Hz, and 0.1 Hz to 0.01 Hz. The ac amplitude was 10 mV. After each set of measurements, the panels were mounted on a rack and taken to the beach corrosion test site and left there for a week. At the end of the week, the panels were brought back to the laboratory for a new set of measurements and the cycle was repeated for up to four weeks of exposure. Subsequent measurements were performed after eight weeks and after one year of atmospheric exposure.

TABLE 1. MATERIALS TESTED, TYPE, RUST GRADE EVALUATION, ZINC CONTENT, AND THICKNESS

COATING	CODE	TYPE	RATING	% ZINC	COATING THICKNESS (µm)
			10.00	NI/A	152
AMERON D-21-9	A	SB	10.00	N/A	102
DEVOE CATHACOAT 302H	В	SB	1.25	N/A	127
SHERWIN WILLIAMS ZINC	С	SB	10.00	N/A	127
CLAD II				NI/A	114
AMERON D-4	D	WB_	9.50	N/A	114
AMERON D-21-5	E	WB_	5.75	N/A	76
BRINER V-65	F	WB	10.00	N/A	
CARBOLINE CZ-D7	G	WB	10.00	N/A	89 89
DuPONT GANICIN 347 WB	Н	WB_	10.00	86	
INORGANIC COATINGS IC-531		WB	9.75	90	89
PORTER TQ-4374H	J	WB	8.63	N/A	76
SOUTHERN COATINGS	K	WB	9.88	90	76
CHEMTEC 600	L	SB	8.75	N/A	89
SUBOX GALVANOX IV	M	SB	8.13	N/A	89
BYCO SP-101	N	SB	10.00	N/A	127
CARBOLINE CZ-11		SB	5.25	84	114
CORONADO 935-152	0 P	SB	10.00	N/A	127
DEVOE-MARINE CATHA-COAT 304		SB	10.00		
GLIDDEN GLID-ZINC 5530	Q	SB	8.50	86	127
GLIDDEN GLID-ZINC 5536	R	SB	2.00	76	102
KOPPER 701	S	SB	7.00	N/A	102
SUBOX GALVANOX V	T	SB	2.75	N/A	102
TNEMEC 90E-75	U	SB	7.00	76	89
GALVANIZED STEEL	Z				
WB = Water-based (inorganic silicate) SB = Solvent-based (ethyl silicate)					

III. RESULTS AND DISCUSSION

Due to the limitations on the length of this paper and the large amount of data generated in this investigation, this discussion will be focused on four coatings that are representative of the group of twenty-one included in this research. A and P were chosen as typical examples of those coatings that have a rust grade evaluation of 10.00 (good performers). R and T were chosen as typical examples of those coatings that had a poor performance (rust grade evaluation of 2.00 and 2.75 respectively).

The variation of the corrosion potential with time of atmospheric exposure for the twenty-one coatings included in this investigation is presented in Table 2. Graphical presentation of the variation of the corrosion potential with time of atmospheric exposure is presented in Figure 2 for coatings A, P, R, and T.

The evolution of the corrosion potential with time is a useful indicator of the galvanic mechanism of protection of the coating. The corrosion potential of steel quoted in various Standards and codes of practice¹⁰ is -0.735 V Ag/AgCl [-0.780 V (SCE)]. At or below this potential the corrosion of the steel is reduced to approximately zero. Coatings A and P exhibit galvanic protection for up to eight weeks at least. Coatings R and T exhibit corrosion potentials above the protection potential for steel after two weeks of atmospheric exposure thus indicating their failure at protecting the steel galvanically. However, corrosion potential variation with time measurements provide no estimate of the performance of the coating after the cessation of the cathodic protection mechanism.

Another indication of the galvanic mechanism of protection is obtained by analyzing the EIS data. Figure 3 is typical of the Nyquist plots obtained for zinc-rich primers upon initial immersion in 3.55% NaCl prior to atmospheric exposure. Since at this time, the coating is protecting the steel galvanically, the Nyquist plot represents the corrosion of the zinc dust in the coating. The magnitude of the diameter of the semicircle is related to the rate of corrosion of the zinc dust: The smaller the diameter, the greater the rate of corrosion of the zinc and its protective galvanic effect. Upon atmospheric exposure, the Nyquist plot evolves to include what has been described as the barrier mechanism of protection. Figure 4 shows the appearance of a second semicircle in the low frequency range of the Nyquist plot. The parameters extracted from this region are associated with the barrier mechanism of protection.

To extract information on the galvanic as well as on the barrier mechanism of protection from the Nyquist plots generated in this investigation, the impedance spectra were analyzed using a computer simulation program¹¹. The equivalent circuit R₁(R₂C(R₃W))¹² shown in Figure 5 provided a satisfactory fit for the data (see simulation curves in Figures 3 and 4). The letters R, C, and W denote a resistor, capacitor, and Warburg impedance respectively.

TABLE 2. VARIATION OF CORROSION POTENTIAL (VOLTS) WITH TIME OF ATMOSPHERIC EXPOSURE

COATIN	INITIAL	ONE WEEK	TWO WEEKS	THREE WEEKS	FOUR WEEKS	EIGHT WEEKS	ONE YEAR
G		*****					
	-1.029	-1.025	-0.980	-0.947	-0.947	-0.898	-0.409
<u> </u>	-0.004	-0.894	-0.143	-0.328	0.002	-0.084	-0.536
В		-1.024	0.110	-0.923	-0.907	-0.836	-0.520
С	-1.015	-0.899	-0.767	-0.816	-0.625	-0.800	-0.727
D	-0.990	-0.552	-0.575	-0.155	-0.248	-0.457	-0.769
E	-0.249		-0.995	-0.976	-0.904	-0.877	-0.561
F	-1.009	-1.030	-0.829	-0.869	-0.789	-0.879	-0.394
G	-0.777	-0.117	-0.029	-0.903	-0.692	-0.853	-0.688
H	-0.895	-0.758	-0.881	-0.867	-0.692	-0.810	-0.720
	-0.846	-0.725	-0.944	-0.935	-0.766	-0.852	-0.414
J	-0.992	-0.982		-0.616	-0.305	-0.499	-0.742
K	-0.524	-0.571	-0.560	-0.935	-0.968	-0.889	-0.603
<u>L</u>	-0.988	-0.999	-0.979	-0.965	-0.718	-0.788	-0.270
M	-1.013	-1.025	-0.964	-0.965	-0.796	-0.925	-0.913
N_	-0.814	-1.021	-1.008		-0.750	-0.862	-0.407
0	-1.035	-1.022	-0.956	-0.926	-0.766	-0.894	-0.449
Р	-0.987	-0.995	-0.939	-0.930		-0.888	-0.393
Q	-1.016	-1.011	-0.957	-0.929	-0.953	-0.909	-0.460
R	-0.768	-1.015	-0.490	-0.771	-0.269	-0.903	-0.524
S	-0.975	-0.999	-0.937	-0.950	-0.821		-0.524
T	-1.002	-1.020	-0.244	-0.584	-0.468	-0.843	-0.336
U	-0.983	-0.686	-0.861	-0.773	-0.520	-0.513	-0.865
Z	-1.024	-0.966	-0.959	-0.959	-0.788	-0.788	-0.005
-							

Table 3 lists the values obtained for R_2 and C for coatings A, P, R, and T. The variation of R_2 with time of atmospheric exposure is shown in Figure 6. During the early stages of atmospheric exposure, R_2 represents the galvanic mechanism of protection involving the corrosion of the zinc. After this period, the resistance is equivalent to the magnitude of the film resistance. Its increase is due to the build up of zinc corrosion products responsible for the barrier effect. This trend holds for coating P (up to 56 days of atmospheric exposure), and for coatings A and T (up to 28 days of atmospheric exposure). The change in the value of R_2 for T was not as gradual as it was for A and

P perhaps resulting in the formation of a barrier that was not as effective in protecting the steel as indicated by the poor performance of the coating.

TABLE 3. EQUIVALENT CIRCUIT COMPONENTS FOR COATINGS P, A, R AND T

Coating	Р	Р	Α	Α	R	R	Т	Т
Days	R ₂ (ohms)	C (Farad)						
0	1.89E+02	5.52E-04	3.72E+02	3.06E-04	1.65E+06	2.78E-10	3.77E+02	2.76E-07
7	4.97E+02	1.03E-05	1.50E+02	1.51E-06	9.28E+02	2.10E-08	5.29E+02	2.80E-07
14	9.88E+02	4.30E-08	1.14E+04	8.66E-10	1.07E+05	2.41E-09	1.68E+06	1.31E-10
21	2.33E+03	1.27E-08	1.14E+04	8.66E-10	4.49E+04	3.81E-09	1.49E+06	2.01E-10
28	3.70E+03	5.23E-09	2.50E+05	2.29E-10	2.98E+06	3.01E-10	1.21E+06	2.18E-10
56	2.58E+04	5.28E-09	1.52E+04	1.37E-08	8.67E+04	3.42E-10	3.51E+03	8.23E-08
365	2.22E+04	2.04E-10	5.19E+04	2.14E-10	5.57E+06	3.59E-10	2.21E+04	2.45E-08

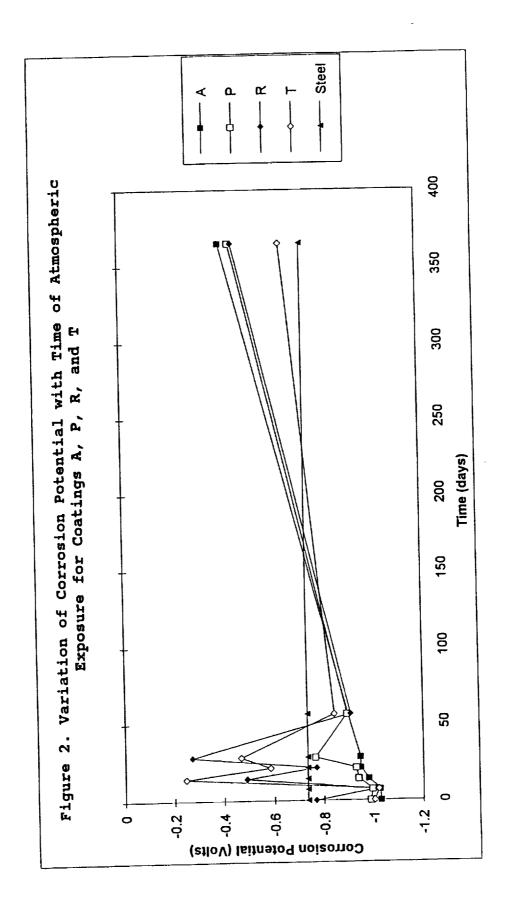
The capacitance variation with time of atmospheric exposure is shown graphically in Figure 7. Coatings A and P exhibit initial capacitances on the order of 10⁻⁴ Farad. Both coatings show a gradual change toward lower values of capacitance in the order of 10⁻¹⁰ Farads. Lower capacitance values can be attributed to a decrease in the water contents of the protective film formed by the zinc corrosion products. Coatings R and T exhibit initial capacitances that are lower than those for A and P. The change in capacitance with time of atmospheric exposure is not as pronounced as it was observed for A and P. This behavior may be attributed to the fact that coatings R and T do not form a barrier that is as effective at protecting the steel as the barrier formed by A and P.

IV. CONCLUSIONS

It has been shown that there is a correlation between the long-term performance of zinc-rich primers and several parameters obtained from EIS measurements in combination with atmospheric exposure. The equivalent circuit $R_1(R_2C(R_3W))$ provided a satisfactory fit for the EIS data. The corrosion potential and the R_2 resistance are parameters indicative of the galvanic mechanism of protection. A corrosion potential below -0.735 V Ag/AgCl [-0.780 V (SCE)] and an R_2 value that starts around 10^{-2} ohms and increases gradually with time of atmospheric exposure is indicative of good galvanic activity that results in the formation of a protective layer that has a higher resistance. The capacitance of the coating is related to the barrier mechanism of protection. Good coatings have capacitances that decrease gradually as the protective film formed by zinc corrosion products becomes less porous. This decrease in porosity is accompanied by a decrease in the water content of the film which results in lower capacitance values. The two coatings with a high rating had capacitance values that varied from around 10^{-4} to around 10^{-10} Farads. The coatings with the low ratings had initial capacitances that were significantly lower than 10^{-4} .

It is suggested that a flow chart based on the above conclusions can be used to predict the long-term performance of inorganic zinc-rich primers. The chart could be used in order to select those coatings that are expected to perform well under atmospheric conditions similar to those present near the Space Shuttle launch site. The chart is being developed and tested with the available data and will appear in Report No. 94-2082, NASA, Kennedy Space Centér, Materials Testing Branch¹³

Figure 1. Exploded View of Model K0235 Flat Cell



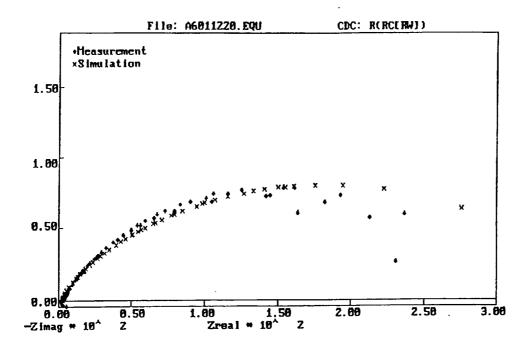


Figure 3. Nyquist Plot for Coating A in 3.55% NaCl prior to Atmospheric Exposure

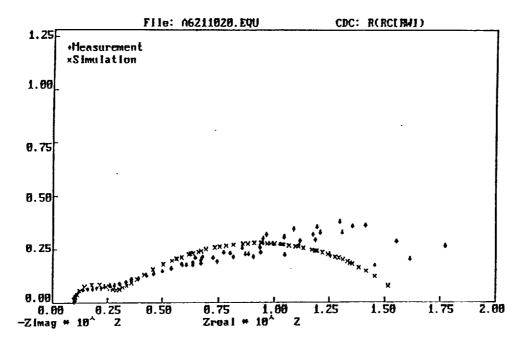


Figure 4. Nyquist Plot for Coating A in 3.55% NaCl after One Week of Atmospheric exposure

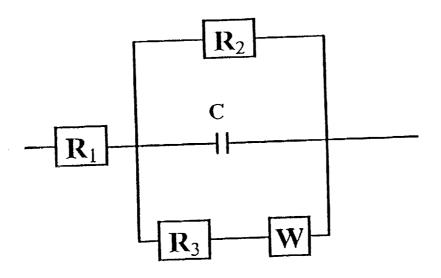
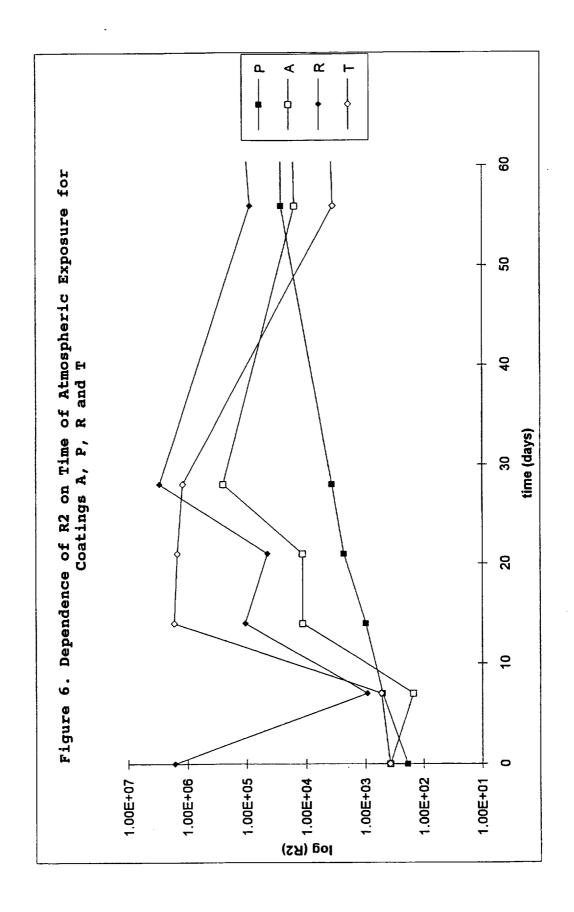
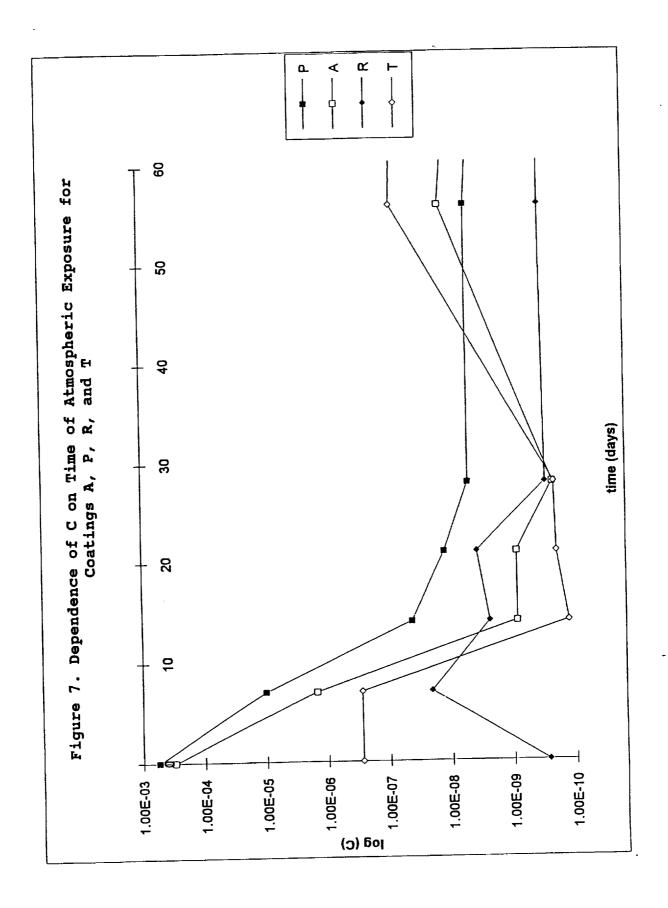


Figure 5. Equivalent Circuit Used to Fit Impedance Data of Inorganic Zinc-Rich Primers





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