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Comparative EIS study of pretreatment performance in coated metals

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Abstract

Various coated metal samples with different pretreatments were investigated by electrochemical impedance spectroscopy (EIS). Variables were the substrate (cold-rolled steel and hot-dipped galvanized steel), phosphate system (iron and zinc phosphate), post rinse (chromate and silane/zirconium rinse) and paint systems. The corrosion performance was determined on the basis of coating degradation, water uptake and interface delamination of the tested samples. The zinc phosphate performed better than iron phosphate on CRS. The silane/Zr rinse did not perform well in the CRS/iron-phosphate system. However, it showed a better performance than the chromate when used as a post rinse of zinc phosphate. Salt spray test (SST) and adhesion test results of the same samples are also reported in this paper and compared to the EIS data. The correlation among three test methods was poor. © 1997 Elsevier Science S.A.

Keywords: Electrochemical impedance spectroscopy; Corrosion; Silane; Interface; Salt spray; Adhesion test

1. Introduction

Electrochemical impedance spectroscopy (EIS) has been shown to be a useful method to study the corrosion performance of polymer-coated metals in recent years [1–3]. Many examples can be found in the literature which illustrate the use of EIS for comparing the performance of different coatings on metals [4–7]. However, the use of EIS to study the effect of pretreatment on the performance of the entire system of metal/pretreatment/coating has only rarely been published [8–11].

The pretreatment of metals before painting usually includes a phosphate conversion layer with a post rinse which has traditionally been an aqueous chromate solution. However, chromate is considered toxic and carcinogenic. As a result, environmental regulations have prompted research and development of non-chromate rinses. Recently, it was reported that a new rinse containing a silane coupling agent and a zirconium compound outperformed chromate rinses of phosphates on cold-rolled steel (CRS) and hot-dipped galvanized steel (HDG) in salt spray tests (SST) [12]. However, SST is known not to correlate well with field performance. Since EIS has been proven to be an effective method to measure the corrosion of coated metals [5], we chose this method to determine the effect of the metal surface pretreatment on the corrosion resistance of the total system and to compare between different pretreatments.

In this paper we report on EIS results of coated CRS and HDG with different pretreatments. The EIS performance of coated metals was compared for iron and zinc phosphate with chromate or silane/zirconium post rinses in order to determine the effectiveness of the pretreatment. We also report on SST and adhesion results of the same systems which were compared with EIS measurements in order to verify whether SST and adhesion tests can discriminate between the pretreatments, and whether these three methods can correlate.

2. Experimental

2.1. Materials and treatments

Standard CRS and HDG (G60) test panels were obtained from Q-Panel Company. Methyltrimethoxysilane (MS) was purchased from Dow Corning and H_2ZrF_6 was from Advanced Research Chemicals. The panels were first

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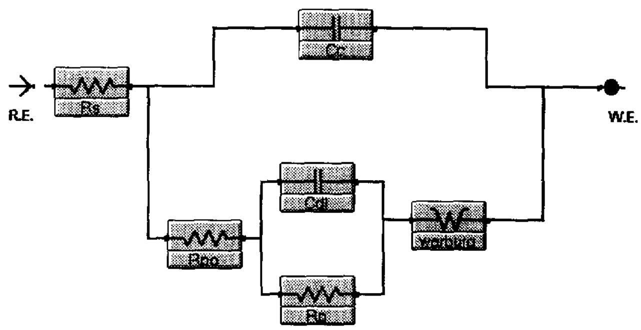

R.E.	Reference Electrode
W.E.	Working Electrode
R_s:	Resistance of electrolyte solution
R_{po}:	Pore resistance of coating
R_p:	Polarization resistance at interface
C_c:	Coating capacitance
C_{dl}:	Double layer capacitance at interface
Warburg:	Diffusion impedance

Fig. 1. Schematic of the equivalent circuit for the coated system.

degreased in an alkaline cleaner, Chem Clean 1328 (Brent America) until a water-break-free surface was attained. The panels to be iron phosphated were then rinsed in tap water and phosphated in a chlorate-accelerated bath. The phosphating bath was operated at 9 points of total acid and pH about 4.8. The pointage of a bath is the number of milliliters of 0.1 N NaOH needed to neutralize a 10 ml aliquot of the bath. After another rinse in tap water, the panels received a post rinse, containing either chromate or silane. The chromate rinse contained 211 ppm Cr(VI) and 193 ppm Cr(III). The bath was run at pH about 4.5. The silane solution contained 0.5% w/w MS and enough H_2ZrF_6 to bring the solution's pH to about 4. The panels treated with the chromate post rinse received a deionized-water post rinse prior to dry-off. All panels were dried at 132°C for about 5 min. The zinc phosphating was similar to the above scenario, with a few additions. Following cleaning and rinsing and prior to phosphating, panels were treated with a titanium activating rinse, whose purpose was to provide convenient nucleation sites for the deposition of zinc phosphate crystals. The zinc phosphate bath was operated at about 20 points total acid and about 2.5 points free acid. Zinc phosphated panels received both types of post rinses, as described above.

Varied deposited weight of the phosphate compounds on the panels was obtained from the different phosphating baths. In iron phosphating, the deposited weight of the phosphate on CRS was estimated as 0.5 g/m^2. The deposited weight of the zinc phosphate on the same substrate was about 2.0 g/m^2, which suggests the zinc phosphate layer was thicker.

Two paint systems were used for coating of the pretreated samples. Iron phosphated CRS panels and zinc phosphated HDG were coated with a blue melamine-modified polyester. A red oxide primer followed by a high-solid polyester was used on zinc phosphated CRS samples. Table 1 is the summary of the phosphate, post rinse and top coat of all the samples.

Table 1

Treatment conditions of samples

Sample ID	Metal	Pretreatment	Post rinse	Paint
A	CRS	Iron phosphate	Cr(VI)/Cr(III)	Blue
B	CRS	Zinc phosphate	Cr(VI)/Cr(III)	Blue
C	CRS	Iron phosphate	MS/Zr	Blue
D	CRS	Zinc phosphate	MS/Zr	Red
E	CRS	Zinc phosphate	Cr(VI)/Cr(III)	Red
F	HDG	Zinc phosphate	MS/Zr	Blue
G	HDG	Zinc phosphate	Cr(VI)/Cr(III)	Blue

Table 2

EIS test conditions

Reference electrode	Ag/AgCl
Counter electrode	Graphite
Electrolyte	NaCl
Electrolyte concentration	1 M (58.44 g/l)
Tested area	4.91 cm^2
Frequency range	0.01–100 000 Hz
AC potential	250 mV
DC potential	0 mV

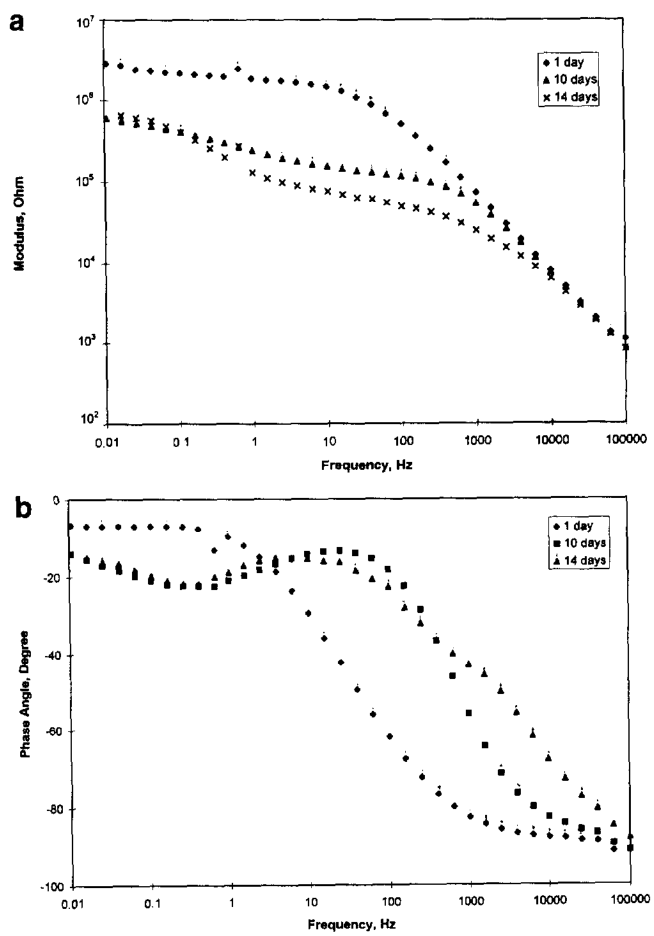

Fig. 2. Bode plot of sample A: (a) impedance; (b) phase angle.

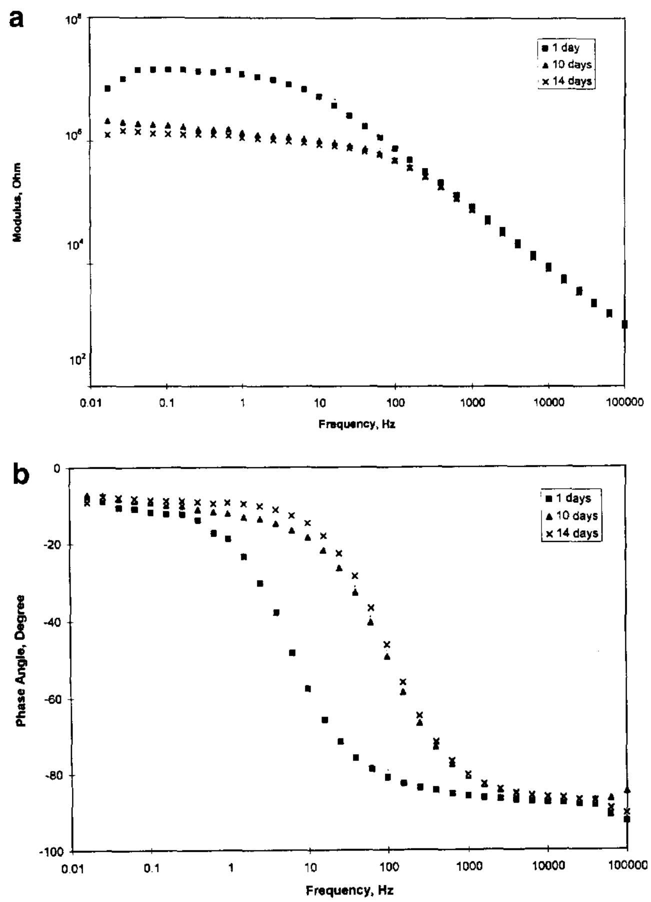

Fig. 3. Bode plot of sample B: (a) impedance; (b) phase angle.

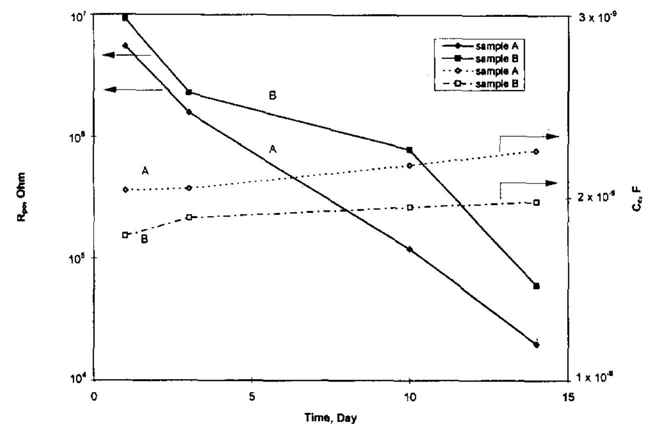

Fig. 4. R_{po} and C_c of samples A and B.

2.2. EIS measurements

The EIS measurements were carried out with a CMS 300 electrochemical impedance system purchased from Gamry Instruments. The measurements were performed under potentiostatic control at the open circuit potential. The test conditions are listed in Table 2.

A glass cylinder of 25 mm diameter was clamped tightly on the panel and was then filled with 1 M NaCl solution to immerse the spot to be analyzed. The salt solution was aerated at all times.

The equivalent circuit model shown in Fig. 1 was employed to analyze the EIS spectra. The circuit consists of working electrode (metal substrate), reference electrode, electrolyte resistance R_s, pore resistance R_{po}, coating capacitance C_c, polarization resistance R_p and double layer capacitance C_{dl}, as well as a Warburg impedance W. The reason for using a Warburg element was that a diffusion feature, a 45° straight line in the Nyquist plot, was found in many EIS spectra. It was found that this model had the best fit to the EIS spectra, compared to the model without Warburg element [11] and the model with a constant-phase-element (CPE), which we reported previously [13]. Values of the elements in the equivalent circuit were determined by fitting the EIS data to the equivalent circuit using the software attached to the instrument. The tolerance of the evaluated data was usually below 0.1%.

2.3. Salt spray test (SST)

The procedure of the SST is based on ASTM B117, except that much of the subjectivity had been removed. A defect was introduced into the painted panels using a scribing tool with a metal tip. The defect was about 10 cm in length and penetrated all the way through to the bare metal.

The salt spray cabinet was operated within the parameters listed in ASTM B117. In general, the test continued until all panels of a set exhibited some measurable amount of creepage.

At the end of the test, panels were removed from the salt spray chamber, rinsed in tap water and dried with paper towels. All loose paint and corrosion products were removed from the panels by means of scraping with the flat end of a spatula or a tape pull. The panels were then evaluated by making measurements of the total width of the

Table 3

EIS results of blue paint, chromate-rinsed CRS samples

Time (day)	A (iron phosphated)					B (zinc phosphated)				
	R_p (Ω) × 10^6	R_{po} (Ω) × 10^6	C_c (F) × 10^{-9}	C_{dl} (F) × 10^{-8}	W (Ω/s$^{1/2}$) × 10^6	R_p (Ω) × 10^6	R_{po} (Ω) × 10^6	C_c (F) × 10^{-9}	C_{dl} (F) × 10^{-8}	W (Ω/s$^{1/2}$) × 10^6
1	1.40	5.50	2.04	160	3.84	1.62	9.21	1.79	2.05	4.83
3	0.62	1.57	2.05	181	2.56	2.18	2.27	1.89	3.34	2.99
10	0.16	0.12	2.18	95.4	0.75	0.59	0.79	1.95	4.51	1.20
14	0.06	0.02	2.26	2.03	0.16	0.25	0.06	1.98	23.9	0.12

Table 4

EIS results of blue-paint, iron-phosphate CRS samples

Time	C (MS/Zr rinsed)				
(day)	R_p (Ω) × 10^6	R_{po} (Ω) × 10^6	C_c (F) × 10^{-9}	C_{dl} (F) × 10^{-8}	W (Ω/$s^{1/2}$) × 10^6
1	0.11	0.86	2.08	35.3	3.17
3	0.10	0.32	2.00	46.6	2.09
10	0.12	0.16	2.26	71.1	0.76
14	0.06	0.02	2.61	1.92	0.23

corrosion creep about the scribe at eight different spots, about 1 cm apart. With three replicate panels for each paint-pretreatment system, the results for the three panels were then averaged to give a final result.

2.4. Adhesion testing

The adhesion of the paint coatings was measured in a pull-off test (ASTM D4541). The test was carried out on an Instron 4465 Universal Testing System using a crosshead speed of 0.5 mm/min. A metal stub was glued to the paint surface using an epoxy-based adhesive cured at room temperature. The total tested area was 5.07 cm^2. The maximum load of each panel was recorded for each sample as a measure of the adhesion of the coating. Two replicate panels were tested for each paint-pretreatment system and the final result was averaged based on the two measurements.

3. Results

3.1. EIS

3.1.1. Effect of phosphate

The Bode plots of CRS sample A and B of Table 1, pretreated with iron or zinc phosphate, chromate rinse and blue coating, are shown in Figs. 2 and 3 as an example. It is clearly observed that the iron phosphated sample corroded

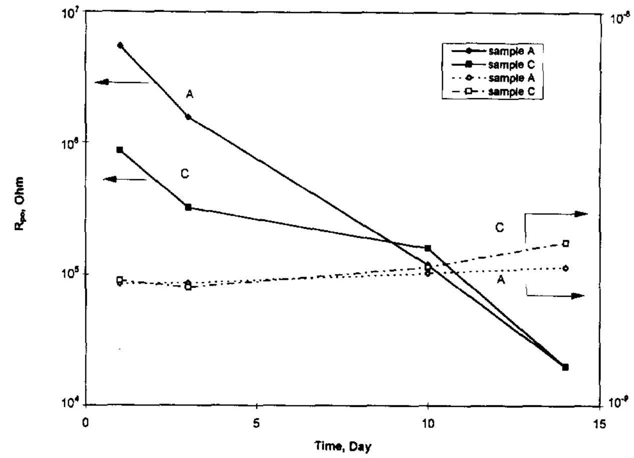

Fig. 6. R_{po} and C_c of samples A and C.

faster than the zinc phosphated sample. Table 3 lists the evaluated element values extracted from the EIS spectra by using the equivalent circuit shown in Fig. 1. The values of the resistances and capacitances of the equivalent circuit elements are plotted in Figs. 4 and 5 for A and B.

The following trend is observed in the results: sample B (zinc phosphate) had higher R_{po} and R_p than sample A (iron phosphate) as can be expected; their difference in R_p was greater than in R_{po}. Its coating capacitance C_c was slightly lower than that of sample A; the C_c of both systems increased slightly with the immersion time; C_{dl} was much higher for sample A than for sample B initially; the C_{dl} of the former decreased with time while an increase in C_{dl} was observed for the latter.

3.1.2. Effect of post rinse

The effect of post rinse on the corrosion properties of the coated metals was also evaluated. Tables 3 and 4 and Figs. 6 and 7 display the EIS results of CRS/iron-phosphate/MS/Zr(or chromate)/blue-coat system (samples A and C). Table 5 and Figs. 8 and 9 are of CRS/zinc-phosphate/MS/Zr(or chromate)/red-coat (sample D and E). The electrochemical results of HDG/zinc-phosphate/MS/Zr(or chromate)/blue-coat (sample F and G) are shown in Table 6 and Figs. 10

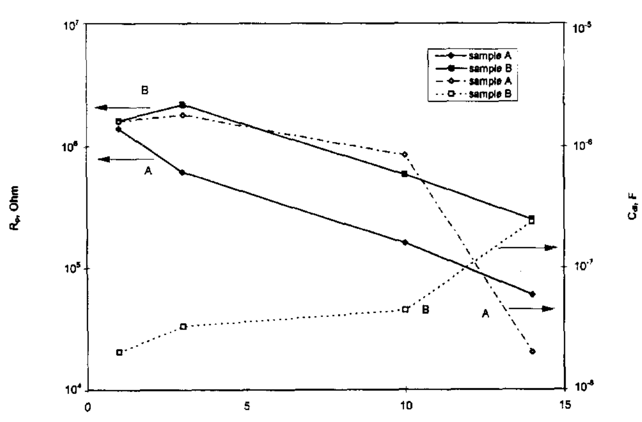

Fig. 5. R_p and C_{dl} of samples A and B.

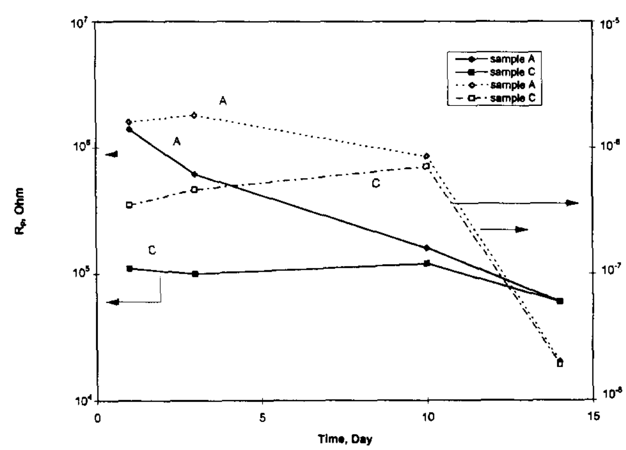

Fig. 7. R_p and C_{dl} of samples A and C.

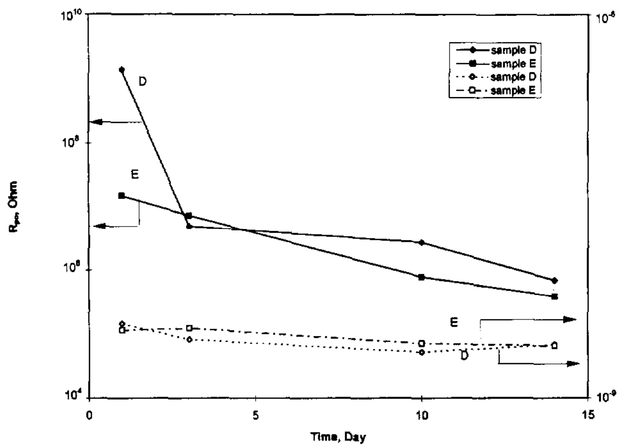

Fig. 8. R_{po} and C_c of samples D and E.

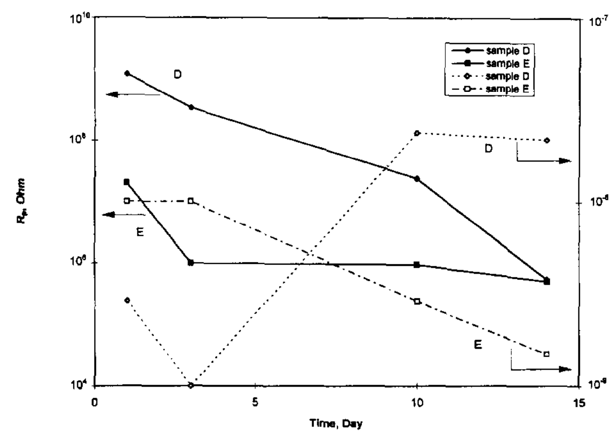

Fig. 9. R_p and C_{dl} of samples D and E.

and 11. The Bode plots of these samples showed trends similar to those shown in Figs. 2 and 3.

Compared with the MS/Zr rinsed sample C, the chromate rinsed sample A displayed higher resistances R_{po} and R_p (Figs. 6 and 7). The coating capacitance C_c of both panels was comparable. Their double layer capacitance C_{dl}, on the other hand, had a similar trend but with different in values; sample C had a lower C_{dl}. Their Warburg values were also very close.

In comparison with zinc phosphated and chromate rinsed sample E, the silane-rinsed sample D demonstrated higher values of R_{po}, R_p and W (Figs. 8 and 9). No significant difference was observed between their C_c values. The C_{dl} of sample D increased with time while that of sample E gradually decreased.

The effect of the paint system is also noticed when comparing the red-painted sample E and blue-painted sample B. Sample E had higher resistances and lower capacitances than sample B.

In the case of the zinc phosphated HDG systems (samples F and G), the MS/Zr-rinsed sample showed higher resistances, especially R_p, than the chromate rinsed sample. The double layer capacitance of the former was lower than the latter. Their coating capacitance and Warburg impedance were similar.

3.2. SST results

Table 7 lists the corresponding SST results of the samples. It was observed that in the cases of samples A and C as well as F and G, the MS/Zr rinsed panels had smaller creepage, i.e. better corrosion performance. In comparison with the chromate rinsed sample E, the MS/Zr rinsed sample D showed a very large creep. At first glance, the correlation between the two methods is poor since in the EIS test sample D had the highest R_p and R_{po} among all the tested samples.

3.3. Adhesion testing

It was observed that in the pull-off test, the iron phosphated samples delaminated in the paint and the zinc phosphated samples delaminated between the phosphate and substrate. The adhesion values obtained from the pull-off test are shown in Table 8. Among all samples, the iron phosphate samples A and C displayed the highest strength. The adhesion strengths of zinc phosphate samples were similar to each other and much lower than those of the iron phosphate samples. Obviously, these results do not correlate with the EIS results.

4. Discussion

4.1. EIS

It is generally assumed that the elements of the equivalent circuit are correlated with the corrosion properties of the

Table 5

EIS results of red-paint, zinc-phosphate CRS samples

Time (day)	D (MS/Zr rinsed)					E (chromate rinsed)				
	R_p (Ω) $\times 10^6$	R_{po} (Ω) $\times 10^6$	C_c (F) $\times 10^{-9}$	C_{dl} (F) $\times 10^{-8}$	W (Ω/s$^{1/2}$) $\times 10^6$	R_p (Ω) $\times 10^6$	R_{po} (Ω) $\times 10^6$	C_c (F) $\times 10^{-9}$	C_{dl} (F) $\times 10^{-8}$	W (Ω/s$^{1/2}$) $\times 10^6$
1	1200	1360	1.56	0.29	300	20.0	15.0	1.50	1.00	8.06
3	339	4.96	1.42	0.10	19.1	1.00	7.36	1.52	1.00	3.15
10	24.3	2.75	1.32	2.38	14.4	0.95	0.79	1.39	0.29	1.50
14	0.56	0.70	1.38	2.19	2.43	0.52	0.39	1.37	0.15	0.26

Table 6

EIS results of blue-paint, zinc-phosphate HDG samples

Time (day)	F (MS/Zr rinsed)					G (chromate rinsed)				
	R_p (Ω) × 10^6	R_{po} (Ω) × 10^6	C_c (F) × 10^{-9}	C_{dl} (F) × 10^{-8}	W (Ω/$s^{1/2}$) × 10^6	R_p (Ω) × 10^6	R_{po} (Ω) × 10^6	C_c (F) × 10^{-9}	C_{dl} (F) × 10^{-8}	W (Ω/$s^{1/2}$) × 10^6
1	66.6	72.2	1.87	0.04	0.25	4.69	9.52	2.01	0.27	0.30
3	50.1	2.20	1.86	0.08	0.012	0.69	1.00	1.84	1.61	0.014
10	0.11	0.14	2.05	1.16	0.002	0.08	0.11	2.08	462	0.004
14	0.03	0.01	3.58	45.5	0.005	0.01	0.006	4.40	165	0.013

system [14–16]: the pore resistance R_{po}, is a measure of the porosity and degradation of the coating; the increase of coating capacitance C_c with time is related to the water uptake of the coating; the polarization resistance R_p and double layer capacitance C_{dl} are two parameters used to specify the delamination of the top coat and the onset of corrosion at the interface [14]. In general, a coated metal system which performs well in corrosion is characterized by high resistances R_{po} and R_p, lower capacitances C_c and C_{dl}, as well as high Warburg impedance W [17], as compared with poor systems.

The trend of C_{dl} is complex. A change in C_{dl} value can be associated with the competition between delamination and corrosion product accumulation at the interface. The C_{dl} value increases as water spreads at the interface and the delaminated area extends. On the other hand, the accumulation of the corrosion product at the interface reduces the area of the double layer capacitor, which will lead to a decrease of the C_{dl} value. Therefore, the change of C_{dl} may depend on which factor, delamination or corrosion product accumulation, was more dominant during the corrosion process. However, it should be pointed out that both increase and decrease of C_{dl} are the results of corrosion development at the metal surface and a constant C_{dl} is an indication of a stable interface.

The Warburg impedance is a function of diffusion thickness and diffusion coefficients of the oxidant and the reductant [18]. A higher Warburg impedance corresponds to a smaller diffusion coefficient or longer diffusion path.

The zinc phosphate sample (sample B) had a less porous and less degraded coating, as well as a more stable and less delaminated interface than the iron phosphate sample A, as shown in Figs. 4 and 5. The slight increase of C_c in both samples indicated a small amount of water uptake. The decrease of C_{dl} in the zinc-phosphated system was mainly caused by the accumulation of corrosion product. In contrast, the iron phosphated sample had an increasing C_{dl} which was interpreted as the delamination on the interface.

The iron and zinc phosphate coatings have different surface composition, surface energy and basicity [19]. The thicker zinc phosphate conversion layer contributed to the higher pore resistance and lower coating capacitance of the coated system. The better interface adhesion in the zinc phosphated system must be related to the surface properties of the phosphate or the absence of pores in the phosphate.

On the iron phosphate, the MS/Zr (sample C) did not work as well as the chromate (sample A) to enhance the coating stability. Considering the interface improvement, the effect of both rinses was comparable: the chromate rinsed A had a higher R_p but the MS/Zr rinsed C had lower C_{dl}. It seems that the MS/Zr was more effective to improve the interface. Both systems exhibited an initial increase followed by a decrease of C_{dl}, which suggests the delamination dominated the early corrosion process and so did the accumulation of the corrosion product in the latter stage.

When used as a rinse of zinc phosphate, however, the MS/Zr rinse showed a better performance than chromate for

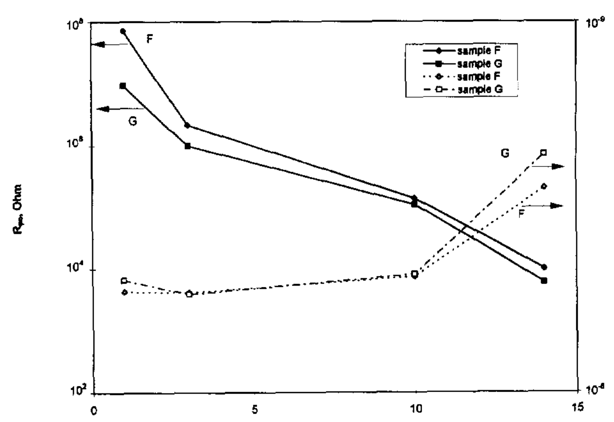

Fig. 10. R_{po} and C_c of samples F and G.

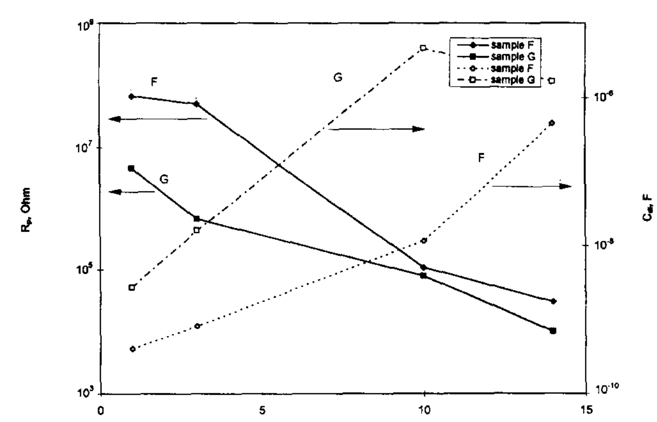

Fig. 11. R_p and C_{dl} of samples F and G.

Table 7

Summary of SST results

Code	Exposure (h)	Creepage (mm)
A	384	3.2 ± 0.4
C	384	2.6 ± 1.4
D	720	6.7 ± 1.3
E	720	2.4 ± 1.1
F	240	1.3 ± 0.4
G	240	3.0 ± 0.3

both CRS (samples D and E) and HDG (samples F and G). The MS/Zr rinse reduced both coating degradation and interface delamination, especially the latter.

The slight decrease of the C_c in samples D and E displayed that there was no significant water uptake. The different trends of C_{dl} of both samples could also be caused by either water spreading or corrosion product formation, as discussed before.

In the case of samples F and G, the slight increase of C_c indicated a small amount of water uptake in the coating layer of this pair of samples. The increase of C_{dl} showed the water spreading dominated the corrosion process. Their Warburg impedances were similar in value.

Figs 12 and 13 present a comparison of the C_{dl} and R_p values of all samples in a linear scale. From the comparisons of C_{dl} and R_p values between samples A and C, D and E, as well as F and G, the improvement of interfacial adhesion due to the MS/Zr rinse is observed more clearly. From the figures, the differences in interface between zinc phosphate and iron phosphate (samples A and B), red paint and blue paint (samples B and E) are also well illustrated. In addition, the trend of the corrosion process is also displayed in Fig. 12: we interpret the curves as an initial delamination (increase of C_{dl}) and a subsequent accumulation of corrosion product at the delaminated interface (decrease of C_{dl}) during the corrosion processes in samples A, C and G.

The trend in R_p is similar for all systems, i.e. a decrease but the rates are different. Sample D has the highest resistance of all samples.

The good corrosion performance of the MS/Zr rinse on

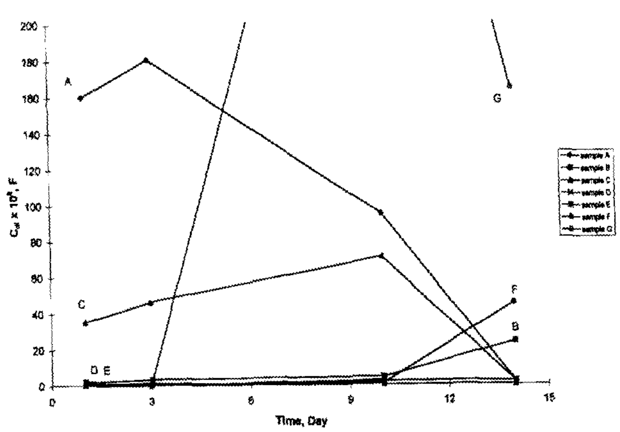

Fig. 12. Comparison of C_{dl} data for all samples.

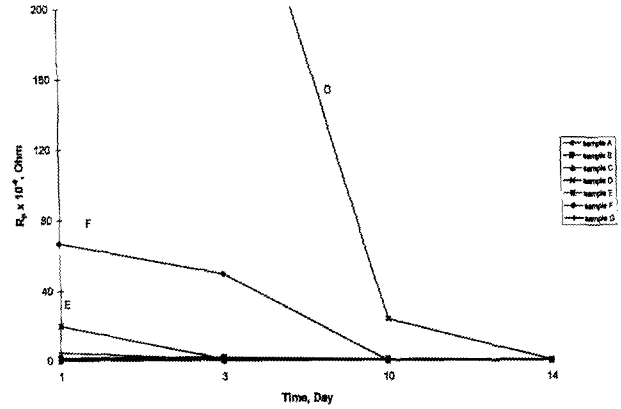

Fig. 13. Comparison of R_p data for all samples.

zinc phosphate suggests that the surface properties of the zinc phosphate are important. It is likely that zinc phosphate crystals are more basic, compared to the iron phosphate crystals, so that zinc phosphate has a stronger interaction with acidic Si–OH groups of MS molecules [19]. It has been pointed out that acid-base reactions across an interface are beneficial to adhesion [20]. The polymerized, crosslinked silane film can delay the attack to the phosphate crystals by corrosion media, such as Cl^-, water and O_2 [21]. The silane film connects to polymer coatings by either covalent bonds or by forming an interpenetrating network [8]. Zirconium compounds have been used as adhesion promoters in the coating industry [22]. The encouraging performance of the silane may lead to the development of a practical replacement for chromate.

4.2. Correlation between EIS and other two tests

The discrepancies between the two corrosion tests can be understood when we compare the processes of corrosion in both tests [23]. Figs. 14 and 15 display schematically the corrosion processes in the EIS and SST tests. In EIS, the undamaged test area is exposed to a 1 M NaCl solution. EIS measures the diffusion of the electrolyte through the coating layer as well as the corrosion and the delamination at the coating/metal interface in a 100% wet solution. In SST, on the other hand, the scribe is exposed directly to the electrolyte. Thus, galvanic corrosion cells are set up immediately.

Fig. 14 illustrates that the corrosion mechanism also var-

Table 8

Adhesion strength from the pull-off test

Sample ID	σ_{max} (kN)	Pulled off area (%)
A	1.13	35
B	0.33	100
C	1.06	40
D	0.26	100
E	0.22	100
F	0.28	100
G	0.24	100

ies with the metal substrate in SST. When a coated iron (CRS) panel is exposed in the SST test, the iron exposed in the scribe acts as the main cathode, but secondary cathodes are set up ahead of the anodic front under the paint. Since the cathode is highly alkaline, the zinc phosphate is attacked [24]. It was pointed out that the ability of a silane to improve wet adhesion was dependent upon pH of application to iron and the Si-O-M bond could hydrolyze at high pH [20]. It thus seems that the MS could not protect against the alkaline attack of the zinc phosphate, which is known to dissolve in alkali, as opposed to iron phosphate which does not dissolve [23]. However, the chromate rinse on zinc phosphate showed such a protection because it was not sensitive to pH. If a coated HDG sample is tested, the cathode is in the scribe and the anode is at front. The anode is slightly acidic and pH is about 6, so here zinc phosphate is not attacked. Then, the silane protects the phosphate and a good corrosion performance is observed.

The iron phosphate formed a thin and porous layer on the CRS substrate with good mechanical strength. The porous surface increased the connection between the paint and the metal, i.e. enhanced the adhesion [25]. The zinc phosphate layer was thicker and the $FeZn_2(PO_4)_2$ crystals in the phosphate layer were brittle [25]. The adhesion strength of the iron phosphate samples could thus be expected to be higher than that of the zinc phosphated samples. Because of these mechanical aspects, a correlation between EIS and adhesion cannot be expected.

5. Conclusions

EIS is an effective tool for studying of the effect of metal pretreatment on corrosion protection of polymer-coated metals. From the simulation of the EIS spectra with an equivalent circuit model, one can compare and rank the efficiency of the pretreatment.

Zinc phosphate outperforms iron phosphate in corrosion performance, showing slower degradation of the coating layer and slower delamination at the coating–metal interface. The difference in the performance appears to be the result of a more stable interface and thicker conversion layer formed in the zinc phosphated system.

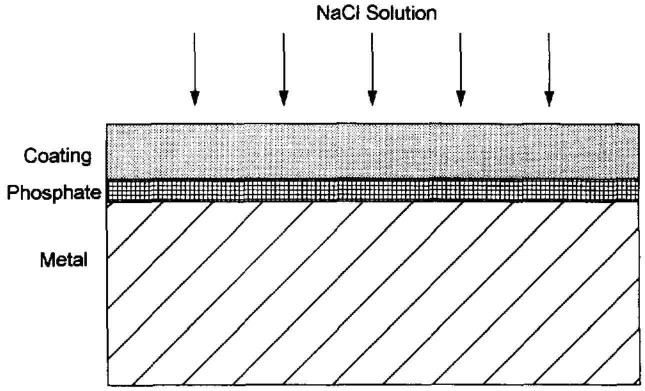

Fig. 14. Corrosion processes in EIS tests.

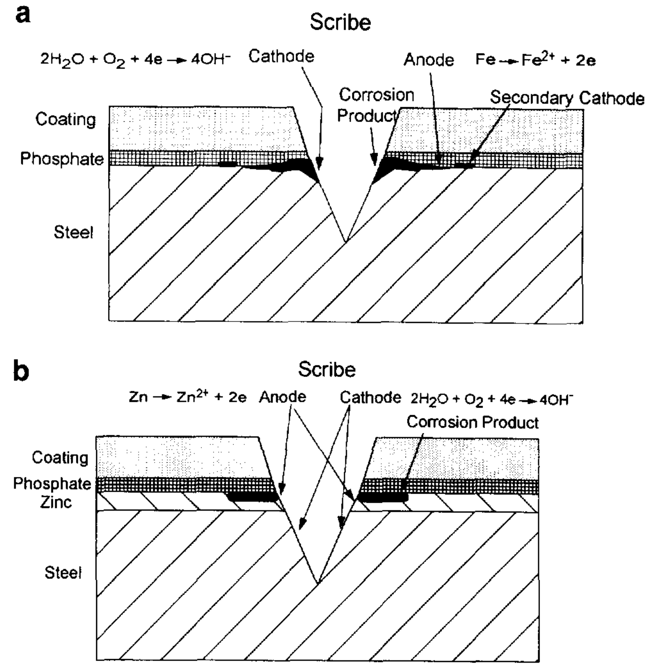

Fig. 15. Corrosion processes in SST tests. (a) CRS, (b) HDG.

MS/Zr rinse as a replacement for the standard chromate rinse does not work as well as chromate on iron phosphate. However, it outperforms chromate on the zinc-phosphated CRS and HDG substrates. In comparison to the chromate rinse, the MS/Zr rinsed sample demonstrated a more stable interfacial layer and a better adhesion. The best corrosion behavior was observed in the CRS/zinc-phosphate/MS/Zr/red-coat system.

In SST, the MS/Zr rinse showed a performance worse than chromate on CRS/zinc-phosphate, presumably because the silane hydrolyzes at high pH resulting in attack of the zinc phosphate by alkali. The MS/Zr treatment displayed better corrosion protection than the chromate on HDG/zinc-phosphate system in this test because the phosphate was not attacked in that case. The poor correlation between EIS and SST in the first case is, in this model, associated with the pH conditions of the two tests.

Iron phosphate samples demonstrated much higher paint pull-off strength than the zinc phosphate samples. There was no significant difference in adhesion strength between the MS/Zr rinse and the chromate rinse. The pull-off test data did not correlate with the EIS results either.

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