



The anti-corrosion performance of water-borne paints in long term tests



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ABSTRACT

One of the most inexpensive and effective method to protect steel against corrosion is paints containing active pigments. The traditional way to test these coatings performance is by accelerated tests (exposition to salt spray and/or humidity chambers) and electrochemical tests (corrosion potential, ionic resistance and electrochemical impedance spectroscopy). However, these tests give incomplete information if the results are not correlated to outdoor or service tests.

The aim of this work was to evaluate water-borne epoxy anticorrosion paints containing different commercial phosphate pigments. The paints were exposed to a semi-industrial atmosphere for 7 years. Electrochemical tests and accelerated assays were also done in order to find a correlation between laboratory and service tests.

The results obtained showed no correlation between those from pigment suspensions and those from painted panels, as it seemed that paint performance is highly dependent on the resin. The pigments zinc iron phosphate and zinc aluminium phosphate performed poorly in pigment suspensions. However, the coatings containing them exhibited the highest ionic resistance, the lowest film capacitance and gave the better results in outdoor tests. Results in outdoor exposure tests correlated with those from impedance measurements.

1. Introduction

Organic coatings are an inexpensive and effective method to protect steel against corrosion. Metals protection by coatings is afforded by two main mechanisms in series: a barrier effect and an anti-corrosion action due to the presence of an active pigment [1–3]. The barrier effect delays water entrance but, once water has reached the metal surface, the anticorrosion pigment action is the main protective effect [2].

The use of inorganic phosphates as active pigments in anticorrosion paint formulations is widespread [4–7]. Although phosphates generally give good results, in certain cases, they proved to have lower performance than zinc chromate [5,8]. As a consequence, diverse strategies were developed to enhance phosphates corrosion protection: particle size reduction, the incorporation of elements such as molybdenum or aluminium as additives, the replacement of phosphate anions by polyphosphate ones, etc. [5,9–14]. These strategies are claimed to yield a pigment which can surpass zinc phosphate performance.

There are different ways to evaluate coatings performance. Accelerated weathering chambers often simulate extreme environments such as marine, high humidity, industrials, etc. However, only a few number of variables are taken into account in these tests (presence of

aggressive ions, high humidity, high temperature, etc.) and, as a consequence, there is not a good correlation between results from these tests and the degradation the coating will suffer under service conditions [15–17]. In this sense, results from outdoor long exposure tests are more reliable because all variables are present and acting together during the exposure period in order to determine coating deterioration [18–20]. However, normally, these assays take longer times than the accelerated ones and they are highly dependent on the testing place.

Electrochemical measurements such as electrochemical impedance spectroscopy (EIS) and electrochemical noise techniques have been used to study metals protection by organic coatings. For example, EIS gives accurate information about film paint characteristics (ionic resistance and film capacitance) and about the corrosion process (charge transfer resistance and double layer capacitance). The variation of these parameters, as a function of the immersion time, gives information about the coating deterioration process [21]. However, these accelerated tests are carried out in immersed conditions and the results are, then, applied to the behavior of the painted metal in a given atmosphere so, it is hard to find out a strict correlation between both type of tests although trends may be predicted [15–17,22,23].

The aim of this work was to evaluate 5 different commercial

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phosphate pigments employed to formulate water-borne epoxy anticorrosion paints which were finally exposed to a semi-industrial atmosphere at La Plata city (geographical coordinates: 34° 54'S and 57° 55'W). Electrochemical tests (EIS) and accelerated assays (salt spray and humidity chamber) were also done in order to find a correlation between laboratory and service tests.

The pigments under evaluation were zinc phosphate, zinc molybdophosphate, zinc aluminium phosphate, zinc iron phosphate and zinc basic phosphate.

Zinc phosphate has been worldwide studied and it appeared as the replacement for zinc chromate [5]. Zinc molybdophosphate and Zinc aluminium phosphate appeared later due to the controversial results obtained with zinc phosphate [5]. Molybdate is an anodic inhibitor whose passivating ability is only less than chromate [24]. Zinc aluminium phosphate enhances corrosion protection by precipitating a phosphate layer [4,24]. This pigment together with zinc iron phosphate and zinc molybdophosphate showed better inhibition than zinc chromate in acidic media due their high solubility in this media [6]. On the other hand, zinc basic phosphate was studied in marine solution with good results [25,26].

2. Experimental

Five anti-corrosion pigments were selected to carry out this research (Table 1). The anti-corrosion properties of the pigments were assessed by electrochemical techniques and, then, waterborne paints were formulated with the selected pigments. Paints anti-corrosion performance was evaluated by accelerated and electrochemical tests and, finally, by an outdoor exposure test. An attempt was done to correlate laboratory tests with the outdoor exposure test.

2.1. Pigments characterization

The selected anti-corrosion pigments were consigned in Table 1 together with their main chemical constituents. Pigments extracts were prepared by dispersing the pigments in distilled water; the pigment:water ratio was 1:10. The dispersion was stirred for 2 h and pH and conductivity were measured after 24 h [27].

The corrosion potential of a SAE 1010 steel electrode was monitored, as a function of time, in the corresponding pigment suspension during 4 h and after 24 h of immersion. The supporting electrolyte was 0.025 M NaClO₄. A saturated calomel electrode (SCE) was used as reference.

Corrosion rates were determined by the polarization resistance technique [28–30] employing the Potentiostat-Galvanostat EG & G PAR Model and a conventional three electrode cell. The working electrode was a SAE 1010 steel rod (area: 0.28 cm²), the reference was the SCE and the counterelectrode a Pt mesh. The supporting

Table 1
pH and conductivity of pigments suspensions.

Pigment	Chemical composition Main constituents	pH	κ (μS cm)
ZP	Zinc phosphate Zn ²⁺ : 42.0%; PO ₄ ³⁻ : 51.0%	6.63	190
ZBP	Zinc basic phosphate Zn ²⁺ : 46.5%; PO ₄ ³⁻ : 39.9%	5.50	37.7
ZFP	Zinc and iron phosphate Zn ²⁺ : 24.2%; PO ₄ ³⁻ : 40.9% Fe: 17.8%	7.67	206
ZAP	Zinc and aluminium phosphate Zn ²⁺ : 33.5%; PO ₄ ³⁻ : 42.7% Al ³⁺ : 2.4	6.68	23.6
ZMP	Zinc molybdenum phosphate Zn ²⁺ : 43.8%; PO ₄ ³⁻ : 35.2% Mo(VI): 0.30%	7.80	832

Table 2
Paints formulation.

Component	% by volume
Anticorrosion pigment	3.5
Barium sulphate	2.2
Talc	2.1
TiO ₂	2.1
Mica	1.8
Resin	65.8
Solvent	20.5
Additives	2.0

electrolyte was 0.5 M NaCl. The sweep amplitude was ± 20 mV o.c. and the scan rate 0.1661 mVs⁻¹. All electrochemical measurements were carried out in normally aerated stirred solutions (300 rpm), after 3 h of immersion of the steel electrode in the pigment suspension.

2.2. Paints composition, preparation and application

Water-borne paints were formulated containing 5.8% by volume, with respect to the total solids content, and represented 30% (v/v) of the total pigment formula (Table 2). This value is often recommended for phosphate pigments [5,24,31]. Titanium dioxide, barium sulphate, talc and mica were incorporated to complete the pigment formula. Mica was added due to its barrier properties and the ability to reduce “flash rusting” [32–34]. The additives (antifoaming, co-dispersant and neutralizing agents) content was 2% v/v.

The film forming material selected to formulate the water-borne paint was an epoxy resin, based on a mix of bisphenol A and bisphenol F. The curing agent (hardener), which also acts as emulsifier, was a modified polyamidoamine with 50% of solids. The resin/hardener ratio was 1.0/1.2 by weight. Neutral demineralized water was employed as solvent. The selected PVC value was 20% in order to enhance the coating barrier properties. Water-borne paint manufacture was carried out employing a high-speed disperser [9,35].

SAE 1010 steel panels (15.0 × 7.5 × 0.2 cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene and then painted by brushing, up to a thickness of 80 ± 5 μm. Painted panels were kept indoors for 14 days before being tested.

2.3. The performance of anticorrosive paints through accelerated tests

A set of three panels was placed in the salt spray chamber (ASTM B 117) to evaluate the rusting (ASTM D 610) and the blistering (ASTM D 714) degrees. Painted panels were evaluated during 4250 h; the mean value of the obtained results was reported in this paper. A similar set was placed in the humidity chamber (ASTM D 2247); and blistering and rusting degrees were evaluated again over the same period of time.

2.4. The performance of anticorrosive paints through electrochemical tests

Impedance measurements of painted panels (frequency range 1.10⁵ Hz ≤ f ≤ 1.10⁻² Hz) were performed in the potentiostatic mode. Measurements were carried out as a function of the exposure time in 0.5 M NaCl, using the 1255 Solartron FRA and the 1286 Solartron EI. The amplitude of the applied AC voltage was 0.010 V peak to peak. Two acrylic tubes were attached to each coated panel (working electrode) with an epoxy adhesive to delimit the measuring area (15.9 cm²). A large area Pt-Rh mesh of negligible impedance and SCE were employed as auxiliary and reference electrodes, respectively. Collected data were interpreted on the basis of equivalent electrical circuits using a suitable fitting procedure developed by Boukamp [36]. These electrochemical experiments were carried out at laboratory temperature (20 ± 2 °C), using a Faraday cage.

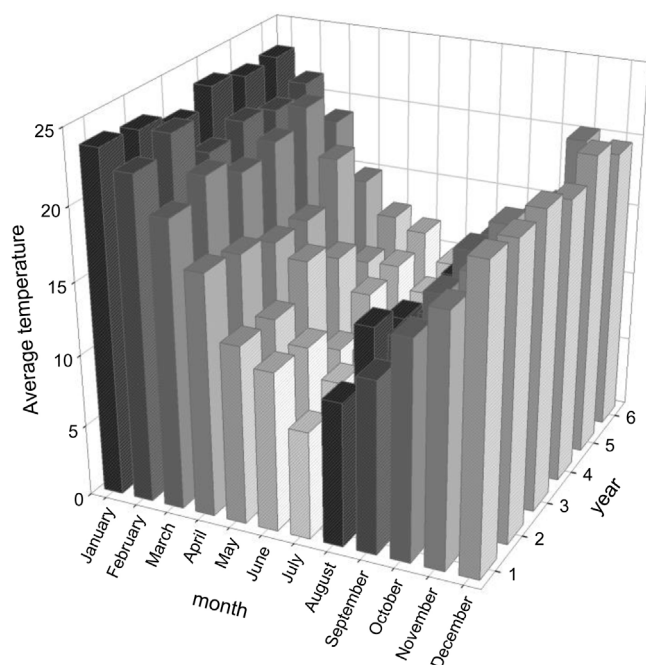


Fig. 1. Average temperature along outdoor exposition.

2.5. The performance of anticorrosive paints in outdoor exposure

Painted panels were exposed at CIDEPIN's experimental outdoor station (geographical coordinates: 34° 54' S and 57° 55' W), in an urban-industrial environment at 45°, facing north. Previously, they were coated with a suitable topcoat up to a final thickness of 100 μm . The characteristics of the station in terms of average temperature, relative humidity, annual rain and winds, along the exposure time, are shown in Figs. 1–4.

3. Results and discussion

3.1. Pigments characterization

The pH and the conductivity (κ) of pigments suspensions may be seen in Table 1. The pH may be related to the ability of the pigment to

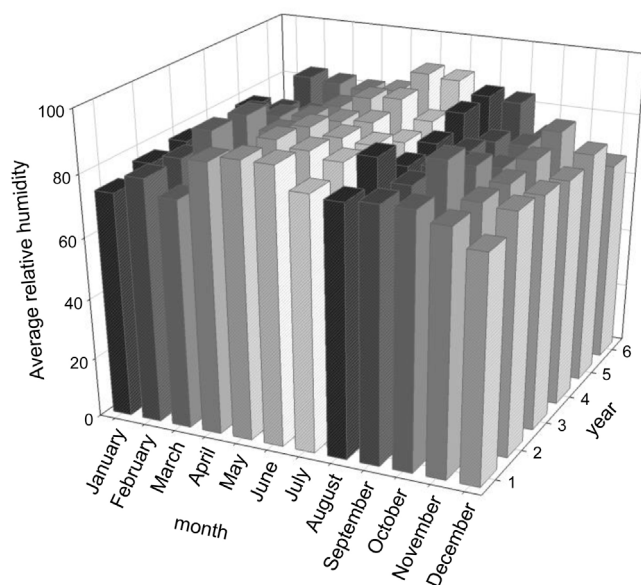


Fig. 2. Average relative humidity along outdoor exposition.

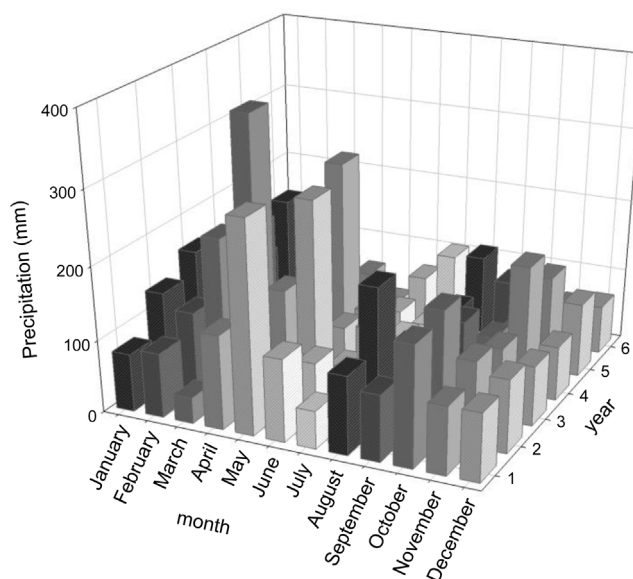
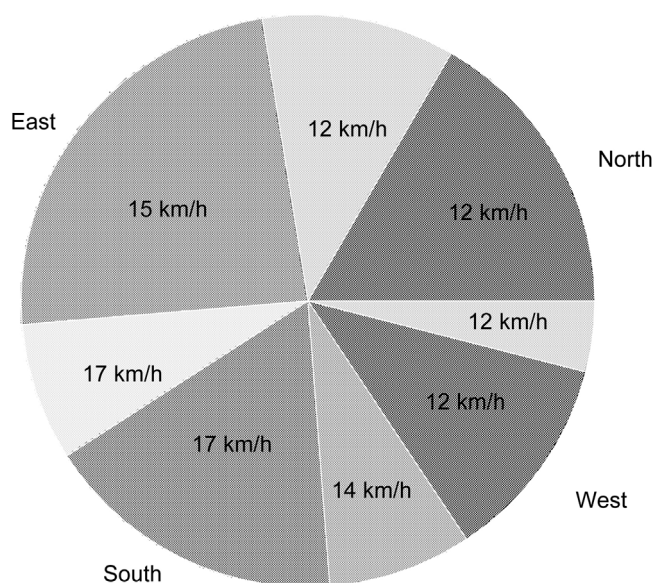


Fig. 3. Average precipitations along outdoor exposition.

Fig. 4. Winds, relative frequency and speed in km h^{-1} .

passivate steel. Steel passivation is accomplished at pH values higher than 7.0 [37]. The suspension conductivity depends on the pigments soluble fraction in which inhibitive species like PO_4^{3-} , Zn^{2+} , etc. may be found. The highest pH values were measured for ZFP and ZMP suspensions which could inhibit steel corrosion. The highest soluble matter content corresponded to ZMP.

The evolution of steel corrosion potential as a function of the immersion time in pigments suspension showed that, except for ZFP, potentials were positively displaced with respect to steel in the supporting electrolyte (Fig. 5). The largest displacement was achieved with zinc molybdenum phosphate. Finally, all curves showed a similar trend in the sense of a reduction in E_{corr} values as time went on. In the case of ZBP, ZAP and ZMP an initial and slight increase in E_{corr} , more or less extended in time, was observed. This fact could be attributed to the ability of the pigment to passivate the steel substrate.

After 24 h of exposure, steel corrosion potential in phosphates suspensions was comprised between -515 and -546 mV and it did not differ significantly from that of bare steel in the supporting electrolyte (-563 mV); however, corrosion spots appeared only on

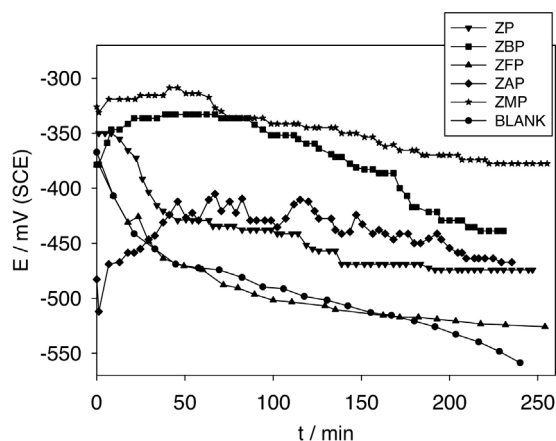


Fig. 5. SAE 1010 steel corrosion potential in pigments suspensions in 0.025 M NaClO₄.

Table 3
I_{corr} of steel immersed in pigment suspension.

Pigment	I _{corr} (μA cm ⁻²)
ZP Zinc phosphate	3.44
ZBP Zinc basic phosphate	3.27
ZFP Zinc and iron phosphate	7.75
ZAP Zinc and aluminium phosphate	24.5
ZMP Zinc molybdenum phosphate	2.60

the control panels. This fact suggested that metal activity was similar in all cases and the protective layer was mainly composed by iron oxides [38], but, in the presence of phosphates this oxide layer was more effective to protect steel. Phosphates are said to plug pores and defects of the protective layer [38]. Metal passivation is reflected in decreased steel corrosion rates (Table 3). In the case of zinc molybdenum phosphate, this reduction was about 25 times with respect to the blank and it was attributed to both, an increase in pH and the relatively high soluble matter content in the pigment extract. ZP, ZBP and ZFP were also effective in restraining steel corrosion rate. The worst anti-corrosion behavior was detected for ZAP (Table 3).

3.2. The performance of anticorrosive paints through accelerated tests

As known, the salt spray test is used to evaluate the anticorrosive performance of a coating in the presence of corrosion stimulating species like chloride ion. However, it was suggested that the humidity chamber is more suitable for the evaluation of waterborne coatings than the salt spray one because there are three processes, concerning the organic binder, which could affect the coating impedance. The first process is related to the penetration of the electrolyte solution into the interconnected macropores of the dry films, the second one consists of polymer swelling accompanied with an increase of the film permittivity. Finally, the long-term slow increase of film conductivity was observed [39,40]. However, results obtained in the humidity chamber revealed that there were not significant differences among the tested paints after 4250 h of exposure (Table 4), independently of the anti-corrosion efficiency of the selected pigments. As the binder was the same for all paints, this chamber could not detect substantial differences in the anti-corrosion behavior of paints.

In change, the exposure in the salt spray test allowed to appreciate some differences in the anti-corrosion performance of the formulated paints which did not depend strictly on the anti-corrosion performance of the pigment but it seemed to depend of the paint as a whole (Table 5). This affirmation sounds reasonable if one takes into account that these paints are normally formulated with a lower PVC value and, as a consequence, the role of the binder becomes important. On

considering the whole paint, new factors, such as the pigment-binder interaction, appeared and could determine coatings performance. The best performance was achieved with the paint pigmented with ZMP and ZP and no significant differences were encountered with the coating containing ZBP, ZFP and ZAP although ZBP exhibited a low steel corrosion rate and the others the higher ones (Table 3).

As a general rule, blistering was detected after 745 h of exposure in the humidity test and did not differ too much from one paint to another. Blistering in the salt spray test appeared lately, beyond 2600 h of exposure (Tables 4 and 5).

3.3. The performance of anticorrosive paints through electrochemical tests

The point of view adopted in this paper was that of Amirudin and Thierry [22,41] in the sense that visual observation of the spectra could not indicate the exact number of time constants involved in the degradation of the organic coating subjected to a corrosive environment, in change the number of these constants must be determined by data analysis rather than by visual observation of spectra. After 24 h, the anti-corrosion paints tested in this research showed an electrochemical capacitive like that depicted in Fig. 6a. In other cases, a capacitive-resistive response like that in Fig. 6b was observed. The situation did not change during the exposure time because the decrease in the barrier effect was slow. As a consequence, experimental data were fitted with the equivalent circuit shown in Fig. 7.

All tested paints showed a certain barrier effect because, in every case, the ionic resistance was higher than 10⁶ Ω cm² (Table 6). Complete barrier effect is achieved when the ionic resistance is higher than 10⁸ Ω cm² [42]. The ionic resistance (R_m) oscillated as time elapsed probably due to temporarily pore plugging by corrosion products. The highest barrier to ions diffusion was provided by paints pigmented with ZFP and ZAP. Their ionic resistance, after 60 days of exposure was, for both paints, 1 × 10⁹ Ω cm² (Table 6) while in the other cases the ionic resistance was lower and varied between 1 × 10⁷ and 3.2 × 10⁷ Ω cm².

The film capacitance (C_m) was, as a general rule, equal or lower than 1.0 × 10⁻⁹ F cm⁻², this fact pointed out that the coatings had none or very few defects (Table 7) [43]. Paints formulated with ZFP and ZAP also showed the lowest paint film capacitance values 1.5 × 10⁻¹¹ and 2.4 × 10⁻¹¹ F cm⁻², respectively; thus indicating that film integrity was highly preserved in these cases [43]. Then, film capacitance increased for paints pigmented with ZBP and ZMP while the paint containing ZP showed the highest value.

3.4. The performance of anticorrosive paints in outdoor exposure

Differences in paints anti-corrosion performance became perceivable from 4 years of exposure on (Table 8). Paint failure took place at a respect to solvent-borne paints [35]. Results obtained in outdoor exposure seemed to be related to film integrity rather than the anti-corrosion properties of the pigments, as it occurred with solvent-borne coatings [35]. In this sense, paints formulated with ZFP and ZAP underwent 7 years of exposure at La Plata site. These paints exhibited the highest ionic resistance values and the lowest film capacity, as it was mentioned above. On the contrary, the paint pigmented with ZP exhibited a lower qualification at rather early exposure times (~5 years) and its evaluation was discontinued; this paint had one of the lowest film resistance value and the highest film capacitance. Results from the salt spray test and from the humidity chamber could not predict satisfactorily the behavior of these paints in outdoor-long-term exposure test. Instead, impedance measurements allowed establish certain differences among the tested paint which seemed to correlate with outdoor exposure better than other laboratory tests.

Table 4

Assessment of the rusting (R, ASTM D 610) and blistering (B, ASTM D 744) degrees of painted panels in the humidity chamber (ASTM D 2247).

Paint/ Pigment	Time (hours)													
	385		745		1415		2015		2600		3070		4250	
	R	B	R	B	R	B	R	B	R	B	R	B	R	B
ZP	10	8MD	10	8D	10	8D	10	8D	10	6D	10	6D	10	6D
ZBP	10	8MD	10	8D	10	8D	10	8D	10	6D	10	6D	10	6D
ZFP	10	8M	10	8MD	10	8MD	10	8MD	10	6D	10	6D	10	6D
ZAP	9	8M	9	8MD	9	8MD	9	8MD	9	6D	9	6D	9	6D
ZMP	10	8MD	10	8D	10	8D	10	7D	10	6D	10	6D	10	6D

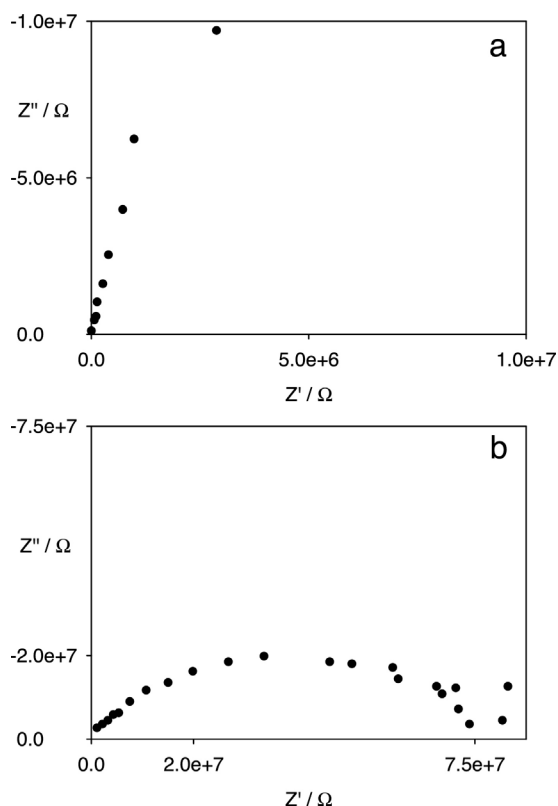
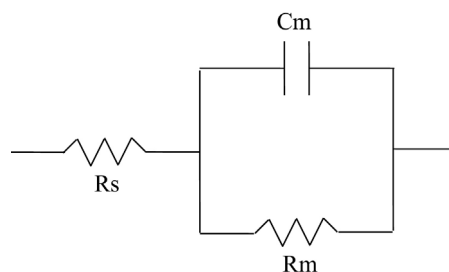
Table 5

Assessment of the rusting (R, ASTM D 610) and blistering (B, ASTM D 714) degrees of painted panels in the salt spray test (ASTM B 117).

Paint/Pigment	Time (hours)											
	385		1055		1415		2015		2600		4250	
	R	B	R	B	R	B	R	B	R	B	R	B
ZP	10	10	10	10	10	10	10	10	10	10	10	6F
ZBP	10	10	10	10	10	10	10	10	10	10	10	8F
ZFP	9	10	9	10	9	10	9	10	9	10	8	6-4F
ZAP	10	10	10	10	9-10	10	8-9	10	8-9	10	7	4F
ZMP	10	10	10	10	10	10	10	10	10	10	9	4F

Rusting degree (ASTM D 610)

Rusting degree	10	9	8	7	6	5	4	3	2	1
% rusted area	No rust	0.03	0.1	0.3	1	3	10	16	33	50

**Fig. 6.** Nyquist's plots of painted panels. Paints formulated with: a) zinc aluminum phosphate, b) basic zinc phosphate.**Fig. 7.** Equivalent circuit to fit EIS experimental data. Rs: solution resistance, Rm: ionic resistance and Cm: paint film capacitance.**Table 6**Variation of paint film resistance (R_m , $\Omega \text{ cm}^2$) as a function of the immersion time in 0.5 M NaCl.

Paint/Pigment	Time (days)				
	0	8	15	30	60
ZP	1.0×10^9	1.7×10^7	2.5×10^7	1.0×10^9	1.0×10^7
ZBP	7.0×10^7	4.4×10^6	6.0×10^6	5.0×10^6	5.0×10^6
ZFP	1.0×10^9	2.2×10^7	3.3×10^7	1.0×10^9	1.0×10^9
ZAP	1.0×10^9	1.6×10^8	2.3×10^7	1.0×10^9	1.0×10^9
ZMP	1.0×10^9	1.7×10^7	2.2×10^7	2.0×10^7	1.0×10^7

4. Conclusion

- As a general rule, phosphates displaced steel corrosion potential to more positive values with respect to the control, SAE 1010 steel in the supporting electrolyte. The best anti-corrosion behavior was observed for zinc molybdenum phosphate and basic zinc phosphate followed by zinc phosphate and zinc aluminum phosphate.
- Steel corrosion rate was reduced by phosphates and the reduction depended on the type of pigment considered. The best anti-corrosion

Table 7Variation of paint film capacitance (Cm, F cm⁻²) as a function of the immersion time in 0.5 M NaCl.

Paint/Pigment	Time (days)				
	0	8	15	30	60
ZP	3.1×10^{-10}	3.5×10^{-10}	3.4×10^{-10}	3.4×10^{-11}	1.0×10^{-9}
ZBP	5.5×10^{-10}	5.4×10^{-10}	6.0×10^{-10}	7.5×10^{-10}	7.5×10^{-10}
ZFP	3.0×10^{-10}	6.0×10^{-10}	7.8×10^{-11}	2.0×10^{-11}	1.5×10^{-11}
ZAP	2.2×10^{-10}	3.4×10^{-10}	5.8×10^{-10}	3.3×10^{-11}	2.4×10^{-11}
ZMP	3.4×10^{-10}	4.7×10^{-10}	5.6×10^{-10}	5.0×10^{-10}	6.2×10^{-10}

Table 8

Rusting degree (ASM D 610) of painted panels after weathering.

Paint/Pigment	Time (years)				
	3	4	5	6	7
ZP	10	8	6	–	–
ZBP	9	9	9	6	–
ZFP	10	10	9	9	6
ZAP	10	10	9	7	6
ZMP	10	10	7	–	–

behavior was observed for zinc molybdenum phosphate, basic zinc phosphate and zinc phosphate.

- The humidity chamber could not differentiate between the protective behavior of different coatings. The behavior seemed to depend on the binder rather than on the pigments anti-corrosion efficiency.
- The salt spray test, in change, showed small differences between the anti-corrosion behavior of different paints. Those containing zinc molybdenum phosphate and zinc phosphate had the best anti-corrosion performance and, in this sense, correlated with results from steel corrosion rate measurements except for basic zinc phosphate.
- Results from EIS measurements do not correlate with those from the humidity chamber and those from salt spray test. They also cannot be compared with results obtained from experiments employing pigment suspensions.
- Water-borne paints had a lower anti-corrosion performance, in outdoor exposure, when compared with solvent borne ones exposed at the same site. The best anti-corrosion behavior was observed for the coating pigmented with zinc iron phosphate followed by the coating containing zinc aluminum phosphate.
- Results in outdoor exposure tests only correlated with those from impedance measurements. The most successful coatings were those which exhibited the highest ionic resistance and the lowest film capacitance; in this case the coating formulated with zinc iron phosphate followed by that pigmented with zinc aluminum phosphate.

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