Performance of Anticorrosive Coatings Containing Tripolyphosphates in Aggressive Environments

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The objective of this research was to study the efficiency of calcium tripolyphosphate and zinc tripolyphosphate as anticorrosive pigments for paints in aggressive environments. Alkyd and epoxy paints, of the solvent-borne type, containing 30% by volume (v/v) of the pigment, were formulated. The pigment volume concentration/critical pigment volume concentration (PVC/CPVC) ratio was fixed at 0.8. In a second stage, water-borne paints containing 30% v/v of both tripolyphosphates and different PVC values (20 and 25%) were also formulated. Finally, standardized accelerated (salt spray and humidity chamber exposure) and electrochemical impedance spectroscopy (EIS) tests were used to assess the protective performance of the coatings. Analysis and interpretation of the experimental data show that both, calcium and zinc tripolyphosphates, inhibit corrosion of painted steel panels exposed to aggressive environments.

Introduction

Traditional anticorrosive paints contain lead or chromium compounds as active pigments; however, these pigments contribute to the environmental contamination and, at the same time, represent a risk to human health.

One of the leading substitutes for these traditional pigments is zinc phosphate, whose protective action was attributed to the formation of an iron oxyhydroxide layer on steel. It can also polarize cathodic areas by the precipitation of sparingly soluble salts, which adhere to the steel surface.[1,2] The low solubility of zinc phosphate and the fact that this pigment was formerly obtained as a coarse crystalline precipitate hindered the growth of effective protective films.[3–6] For improved anticorrosive performance modified zinc phosphates were developed; these modifications involved smaller particle size and the addition of suitable cations.[7–9]

Inorganic tripolyphosphates constitute a promising novel group of nontoxic phosphate inhibitors for paints. Tripolyphosphate anion ($P_3O_{10}^{5-}$) is said to react with iron ions, produced at anodic sites, to yield an insoluble layer containing, mainly, ferric tripolyphosphate. This phosphate coating is very hard and exhibits excellent adhesion onto the steel substrate.[10,11] Since tripolyphosphate anion is of the condensation type, depolymerization takes place in aqueous solution generating species of lower molecular weight such as pyrophosphate and orthophosphate, which react with the coated surface forming an excellent protective film.[12,13]

Aluminum tripolyphosphate was the pioneer of this series, but it has an intrinsic problem due to its high acidity. On account of this, it must be neutralized to yield the formation of an effective protective layer. When aluminum tripolyphosphate is used in anticorrosive paints, the neutralizing substances must be carefully selected to regulate the pH of the pigment formula. The incorporation of pigments with barrier properties, such as silica, is also recommended; they contribute to pore sealing rendering a more impervious film.[14] Previous investigations revealed that calcium tripolyphosphate (CaTPP) and zinc tripolyphosphate (ZnTPP) could be also used in paint formulations.[15–17]

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Metallic ions from different phosphates usually enhance the anticorrosive properties of phosphates in two different ways. One of them is related with soap formation among cations and reactive binders, such as alkyds, which, in turn, form a hydrophobic film on the metal substrate.[18,19] In addition, cations could precipitate sparingly soluble salts on cathodic sites inhibiting oxygen reduction.[2] This last behavior was also observed with phosphonates which are used in neutral aggressive media to protect mild steel. The presence of zinc ions in the solution enhances the protection afforded by these compounds due to the precipitation of a zinc hydroxide film on the metallic substrate.[20–22]

The objective of this research was to characterize the anticorrosive behavior of CaTPP and ZnTPP in solvent and water-borne paints by accelerated (salt spray cabinet and humidity chamber exposure) and EIS tests, when exposed to aggressive environments. Both tripolyphosphates were prepared in the laboratory and their corrosion inhibitive properties assessed, in chloride containing media, using electrochemical techniques, previous to paint elaboration.

Experimental Details

Pigment Preparation. ZnTPP was obtained by mixing, into a glass container, two aqueous solutions; one of 0.1 N sodium tripolyphosphate and the other 0.1 N zinc nitrate. The pH of both solutions was previously adjusted to 4. To accomplish full precipitation of ZnTPP, the pH was finally adjusted to 5.1 by adding 20% sodium hydroxide solution. Then, the resulting solid was filtered employing a Büchner funnel, washed three times with distilled water, dried in air, and washed again twice by suspending it in distilled water. CaTPP was prepared in a similar way, but employing 0.1 N calcium nitrate and adjusting the final pH to 6−8 with 20% sodium hydroxide solution.

As a general rule, tripolyphosphates must not be dried by heating since the anion undergoes self-hydrolysis, the hydrolysis rate being dependent on both the pH of the medium and its temperature. It has been established that at pH 5 and room temperature, the half-life of the anion is 10 000 h (more than a year); but at 80 °C it lasts only 5 h.[12]

Decomposition of tripolyphosphate would also occur in solution and in a dry paint film. However, the products obtained

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Table 1. Composition of Solvent-Borne Paints as Percentage by Volume of Solids

component	paint 1	paint 2	paint 3	paint 4
calcium tripolyphosphate	14.1	14.1		
zinc tripolyphosphate			14.1	14.1
barium sulfate	17.9	17.9	17.9	17.9
talc	7.3	7.3	7.3	7.3
titanium dioxide	7.0	7.0	7.0	7.0
alkyd resin	53.7		53.7	
epoxy/polyamide resin		53.7		53.7
anticorrosive pigment/total pigment (v/v)	30	30	30	30

from this decomposition must be, necessarily, phosphates, and phosphates do protect steel. The only problem in dry paint film could be that soluble phosphates may be formed and may be lixiviated from the film. This seems not to be a problem in this case, because, as it will be seen in the results, the pigments inhibited corrosion.

Pigment Characterization. Pigment composition was established employing current analytical techniques. Physicochemical properties of Ca and ZnTPP, relevant to paint technology, such as density (ASTM D 1475) and oil absorption (ASTM D 281), were determined according to standardized procedures. The pH, conductivity, and ionic composition of the aqueous saturated solution were also determined.

Evaluation of the Inhibitive Properties of Tripolyphosphate Suspensions. The inhibitive properties of both tripolyphosphates were evaluated by measuring the corrosion potential (E_{corr}) of SAE 1010 (UNS G10100) steel electrodes (low surface roughness, mean peak-to-valley height 1.40 μm), as a function of time, in the corresponding pigment suspension. A saturated calomel electrode (SCE) was used as reference, and the electrolyte was 0.025 M NaCl.

The steel corrosion rate in both pigment suspensions, in 0.5 M NaCl, was obtained from polarization resistance measurements. A SCE and a platinum grid were used as reference and counterelectrodes, respectively. The swept amplitude was $\pm$20 mV from the open circuit potential and the scan rate 0.250 mV s^{-1}. Measurements were carried out with a Potentiostat/Galvanostat EG&G PAR Model 273A plus SOFTCORR 352 software. Anodic and cathodic polarization curves, in a wider potential range, were also obtained employing a similar electrochemical cell.

Formulation, Elaboration, and Application of Paints. The resins employed to formulate solvent-borne paints were as follows: a medium oil alkyd (50% linseed oil, 30% *o*-phtalic anhydride, 8% pentaerythritol and glycerol and 12% pentaerythritol resinate) and a bisphenol epoxy−polyamide resin (1:1 ratio v/v). The solvent employed in the former case was white spirit while the mixture xylene/methyl isobutyl ketone/butyl cellosolve (13/45/42%, by weight, w/w) was used for the epoxy paint. It was decided to check the anticorrosive properties of the pigments employing solvent borne paints because their behavior has been well documented for many years. The PVC/CPVC relationship was 0.8 as suggested elsewhere.[23]

The anticorrosive pigment load was 30% v/v of the total pigment content, the same pigment content suggested when orthophosphates are employed as anticorrosive pigments.[7–9] Titanium dioxide, barium sulfate, and talc were incorporated to complete the pigment formula. All pigments were dispersed for 24 h in the vehicle, employing a ball mill, to achieve an acceptable dispersion degree.[24] Paints formulations are shown in Table 1.

An epoxy resin, based on a mix of bisphenol A and bisphenol F (Araldite PY 340-2 form Ciba),[25] was chosen to formulate water-borne paints. The curing agent (hardener), which also acts as emulsifier, was a modified polyamidoamine with 50% of solids. The curing agent employed was Hardener HZ 340,[25] also from Ciba. The resin/hardener ratio was 100/120 w/w. Distilled water was employed as solvent.

Table 2. Composition of Water-Borne Paints as Percentage by Volume of Solids

component	paint 5	paint 6	paint 7	paint 8
calcium tripolyphosphate	5.9	7.4		
zinc tripolyphosphate			5.9	7.4
barium sulfate	3.8	4.8	3.8	4.8
talc	3.4	4.2	3.4	4.2
titanium dioxide	3.5	4.4	3.5	4.4
mica	3.1	4.1	3.1	4.1
hardener/resin (1.2/1 ratio)	78.3	73.1	78.3	73.1
additives	2.0	2.0	2.0	2.0
PVC	20	25	20	25
anticorrosive pigment/total pigment (v/v)	30	30	30	30

The anticorrosive pigment content was 30% of the total pigment content, and titanium dioxide, barium sulfate, talc, and mica were incorporated to complete the pigment formula. Mica was added to the formulation due to its barrier properties and ability to reduce the "flash rusting" degree.[26] Two PVC values, 20 and 25%, respectively, were chosen to enhance the barrier effect of the coatings. Paint composition is shown in Table 2.

Water-borne paints were prepared in a high-speed disperser. Preliminary tests showed the advantage of incorporating the pigment into the hardener, instead of mixing it with the resin. The relatively high viscosity of the hardener made it necessary to add, first, the water and then the pigments in accordance with their increasing oil absorption index; mica was added at last to avoid the break-up of laminar particles.

SAE 1010 steel panels (15.0 $\times$ 7.5 $\times$ 0.2 cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene, and then painted, by brushing, to reach a dry film thickness of 80 $\pm$ 5 μm. Painted panels were kept indoors for 140 days before testing.

Performance of Anticorrosive Paints in Accelerated and Electrochemical Tests. A set of three panels was placed in the salt spray chamber (ASTM B-117). Rusting (ASTM D-610) and blistering (ASTM D-714) degrees were evaluated after 700, 1200, and 2400 h of exposure, respectively. The adhesion of coatings to the steel substrate was measured by the cross-cut tape test (ASTM D 3359) at 0, 24, and 380 h of exposure in this chamber. Another set of panels was placed in the humidity chamber at 38 $\pm$ 1 °C (ASTM D 2247); again, rusting and blistering degrees were assessed over time after 400 and 900 h.

Impedance spectra of painted panels (frequency range 1×10^{-3} Hz $\leq f \leq 1 \times 10^{5}$ Hz) were performed in the potentiostatic mode, at the corrosion potential. Measurements were done as a function of the exposure time to the electrolyte solution, 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 perform the electrochemical measurements in duplicate. The geometric area exposed to the electrolyte, in each cell, was 15.9 cm^2. A large area Pt−Rh mesh of negligible impedance and a SCE were employed as auxiliary and reference electrodes, respectively. The electrolyte was a 0.5 M NaCl solution, whose pH was adjusted to 8.2 with sodium bicarbonate. The experimental impedance spectra were interpreted on the basis of equivalent electrical circuits using a suitable fitting procedure developed by Boukamp.[27]

Table 3. Physical and Chemical Properties of Calcium Tripolyphosphate and Zinc Tripolyphosphate

	solid					aqueous extract		
	composition					solubility (ppm)		
inhibitive pigment	M^{2+} (Ca or Zn)	PO_4^{3-}	Na^+	density, g mL^{-1}	oil absorption, mL g^{-1}	M^{2+} (Ca or Zn)	PO_4^{3-}	pH
calcium tripolyphosphate	22.3	69.7	8.0	2.11	0.62	12.6	43.5	5.48
zinc tripolyphosphate	37.9	59.1	3.0	2.08	0.56	4.3	5.76	5.75

The electrochemical experiments were carried out at laboratory temperature (20 ± 2 °C), using a Faraday cage.

Performance of Anticorrosive Paints during Natural Weathering. It was decided to include partial results obtained in a long-term test, as a consequence of the blistering process observed in the salt spray and humidity chambers, to eliminate any doubts about pigments performance. A set of three panels was coated with each anticorrosive paint. Afterward, the panels were coated with a finishing paint. The thickness of the total coating system was 100 μm. The rather low thickness of the finishing coating would allow the early detection of blistering.

The panels were exposed in an industrial area located at La Plata city, Argentine. The mean concentration of pollutants in the atmosphere are VOC (volatile organic compounds) = 136 ± 78 $\mu g/m^3$; CO = 1.82 ppm; NOx = 25.62 ppb; H_2S = 0.53 ppb, and SO_2 = 0.55 ppb. Average values for relative humidity, temperature, and precipitation are respectively 77.5%, 16.8 °C, and 1268 mm.

Results and Discussion

Pigment Characterization. The physical and chemical properties of CaTPP and ZnTPP are summarized in Table 3. The chemical analysis of the solids revealed that the pigments formulas are as follows: $Ca_2NaP_3O_{10}\cdot 2H_2O$ for CaTPP and $Zn_2NaP_3O_{10}\cdot 2H_2O$ for ZnTPP.

The pH value of the pigment suspension was lower than the pH of the zinc phosphate suspension (6.68) and higher than that of AlTPP (3.26), but this difficulty may be overcome by carefully selecting the complementary pigments.[28,29] The solubility of both tripolyphosphates was found to be higher than that of zinc phosphate, measured in the same conditions.

Evaluation of Inhibitive Properties of Tripolyphosphate Suspensions. E_{corr} of steel, in contact with CaTPP suspension, remained close to ∼−0.645 to −0.640 V during the first four hours of immersion. The behavior of ZnTPP approached that of classical inhibitors since E_{corr} evolution described a very broadband pointing to more positive values; however, the shifting to positive values was of small amplitude (Figure 1). After 24 h of exposure E_{corr} of steel in contact with CaTPP suspension did not change significantly (∼−0.645 V) and was slightly more positive than the value obtained with ZnTPP (∼−0.660 V). These values are not very different from those acquired by the steel electrode in 3% NaCl (∼−0.650 to −0.750 V), suggesting that the protective layer generated by phosphates was constituted by oxyhydroxides, as in the case of orthophosphates.[1,15,17,30] In spite of the corrosion potential values recorded for the steel electrode, in the presence of tripolyphosphates, the metal surface did not show spots or films of red iron oxide and seemed to be passivated. However, if the exposed surface was left one day in the laboratory atmosphere, small red spots begun to appear.

The steel corrosion rate, in pigment suspensions in 0.5 M NaCl, was calculated from polarization resistance measurements at two different exposure times. The values obtained for the CaTPP suspension were 11.5 μA cm^{-2} (3 h) and 11.8 μA cm^{-2} (24 h). The steel corrosion rate in ZnTPP suspension was lower and equal to 9.92 μA cm^{-2} after 3 h of exposure and decreased to 4.36 μA cm^{-2} after 24 h. The steel corrosion rate in the supporting electrolyte was, at least, 10 times higher: 123 μA cm^{-2} after 3 h and 173 μA cm^{-2} after one day of exposure. In brief, the steel corrosion rate was significantly lowered in the presence of both tripolyphosphates, but ZnTPP proved more effective than the calcium salt in restraining steel corrosion. It is also noticeable that, after 24 h of exposure, the steel corrosion rate diminished in the presence of ZnTPP while it increased slightly when CaTPP was the inhibitor. This fact was reflected in the behavior of paints in accelerated tests and EIS.

The inhibition of steel dissolution by tripolyphosphates may be appreciated, as time elapsed, from the analysis of anodic polarization curves. After 3 h of immersion, the curves for both tripolyphosphates have a similar profile in the vicinity of the corrosion potential. At higher potential values, the dissolution of the electrode in the supporting electrolyte seemed to be under ohmic control due to the film formed on the electrode surface (Figure 2). The lowest dissolution current was observed with CaTPP, and the highest one was that of the SAE 1010 (UNS G10100) steel electrode in the supporting electrolyte while ZnTPP exhibited an intermediate behavior. Although currents were very high after 3 h of immersion, they diminished after 24 h of exposure due to the growth of the protective film (Figure 3). The steel electrode immersed in the CaTPP suspension showed a very low current in a wide potential range. In change, current observed for zinc tripolyphosphate suspension was higher, although steel dissolution seemed to be under ohmic control. Evidently, the formation of a layer of corrosion products restrained steel dissolution, and the protective film formed in the presence of CaTPP seemed to be more effective that the film generated by ZnTPP. In every case, the curves correspond-

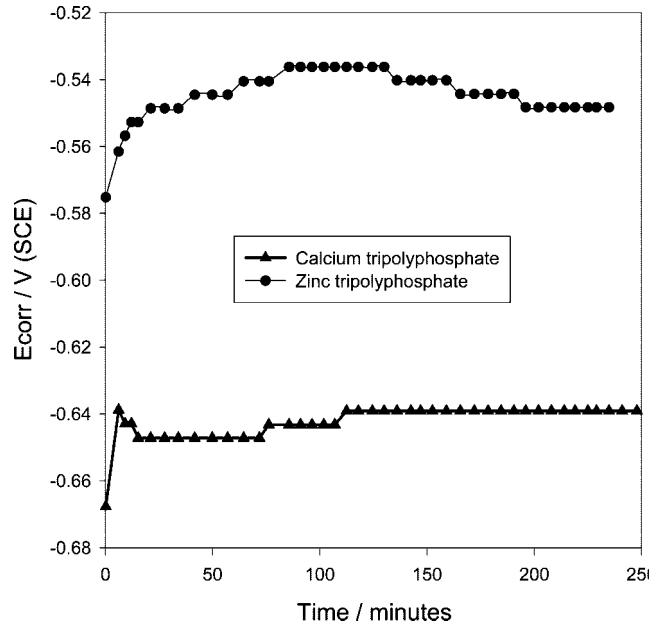

Figure 1. Corrosion potential of steel in calcium tripolyphosphate and zinc tripolyphosphate suspensions. Electrolyte: 0.5 M NaCl.

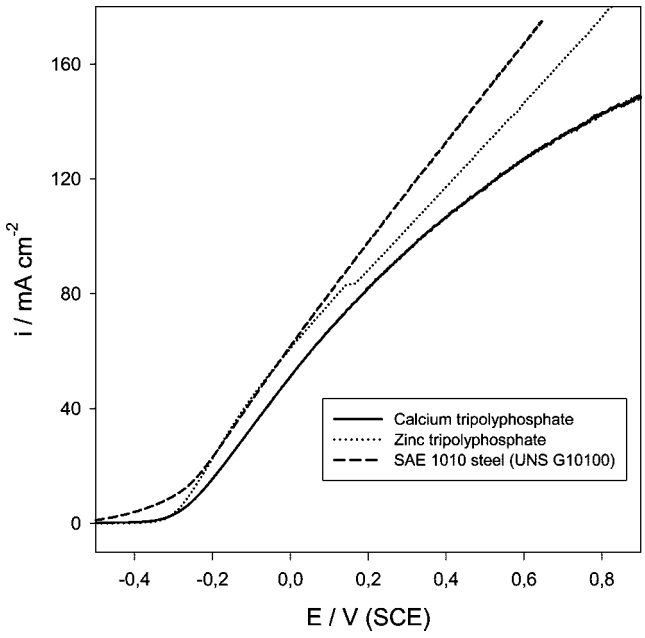

Figure 2. Anodic polarization curves of the SAE 1010 steel (UNS G10100) electrode in the pigments suspensions after 3 h of exposure. Electrolyte: 0.5 M NaCl. Scan rate 3 mV s^{-1}.

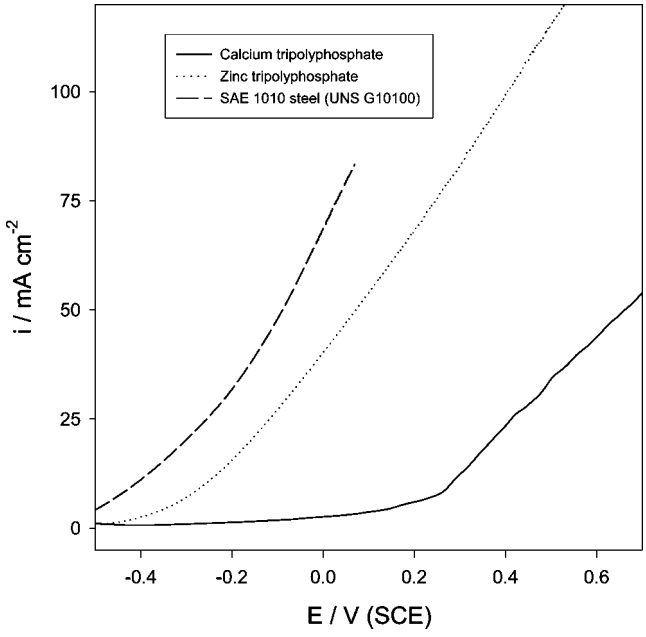

Figure 3. Anodic polarization curves of the SAE 1010 steel (UNS G10100) electrode in the pigments suspensions after 24 h of exposure. Electrolyte: 0.5 M NaCl. Scan rate 3 mV s^{-1}.

ing to the oxidation of the steel electrode in the presence of the supporting electrolyte must be interrupted before the end of the run due to the high amount of iron which passed into solution.

The anodic curves obtained in chloride containing media are quite different from those obtained in previous research with sodium perchlorate as supporting electrolyte.[15–17] In this last case, peaks denoting passivity were clearly observed, and the currents involved in steel oxidation were sensibly lower. Obviously, the presence of chloride changed the characteristics of the protective layer formed on steel.

The cathodic curves did not reveal a significant decrease in the oxygen reduction current due to the presence of tripolyphosphates, as it was observed with different phosphates in

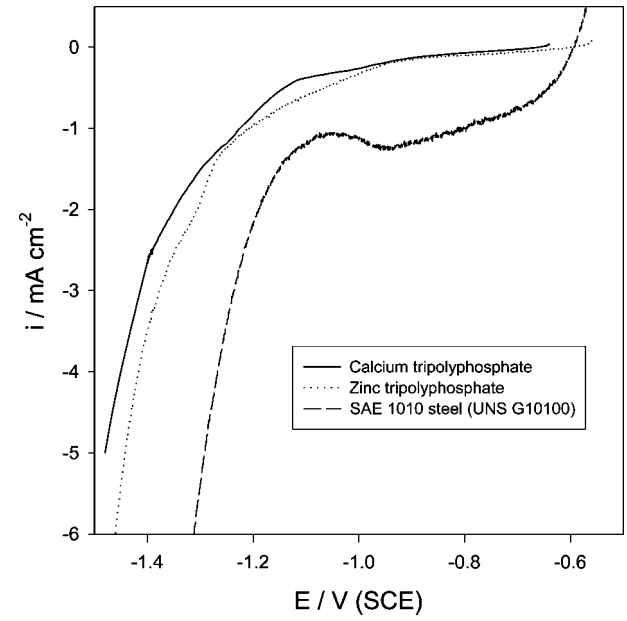

Figure 4. Cathodic polarization curves of the SAE 1010 steel (UNS G10100) electrode in the pigment suspensions after 3 h of exposure. Electrolyte: 0.5 M NaCl. Scan rate 3 mV s^{-1}.

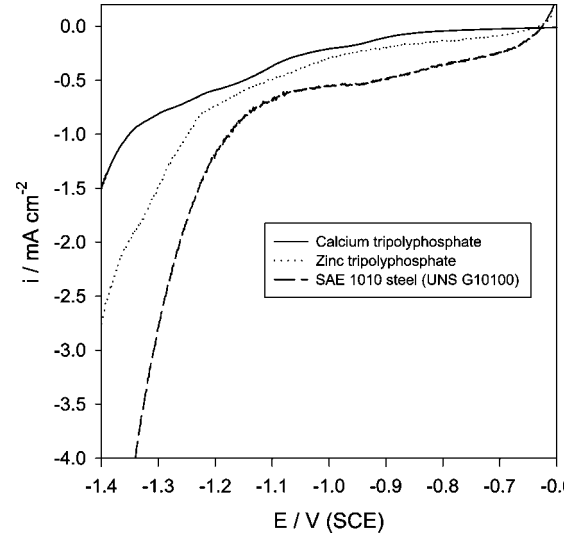

Figure 5. Cathodic polarization curves of the SAE 1010 steel (UNS G10100) electrode in the pigment suspensions after 24 h of exposure. Electrolyte: 0.5 M NaCl. Scan rate 3 mV s^{-1}.

nonaggressive media.[1] The oxygen reduction current in the supporting electrolyte was abnormally high maybe due to the overlapping with the oxide reduction reaction (Figure 4). After 24 h of exposure, the oxygen current on steel, passivated with both tripolyphosphates, did not change significantly, but it was lower in the supporting electrolyte which may be attributed to the accumulation of corrosion products on active sites located at the steel surface (Figure 5).

Performance of Anticorrosive Paints in Accelerated Tests. As it could be expected from the intrinsic differences between the resins employed to formulate solvent-borne paints, the epoxy paints exhibited better performance (Table 4). Both alkyd paints (paints 1 and 3) showed an acceptable behavior after 2400 h of exposure in the salt spray chamber. Instead, both epoxy paints (paints 2 and 4) presented a very good anticorrosive behavior for the same exposure time. The alkyd paint formulated with ZnTPP performed slightly better than the

Table 4. Rusting and Blistering Degrees of Painted Panels after the Salt Spray Test

	hours of exposure					
	700		1200		2400	
paint	rusting	blistering	rusting	blistering	rusting	blistering
1	9	4F	7	4MD	6	
2	9	10	8−9	7F	8	6MD
3	8	6D	7	4F	6−7	
4	9	10	8	10	8	6MD
5	10	8M	7	6M	6	4MD
6	10	6M	8	4MD	6	2D
7	10	6F	10	6F	10	6F
8	10	6F	10	6F	10	6F

Rusting Degree (ASTM D 610)

rust grade	10	9	8	7	6	5	4	3	2	1
rusted area, %	not rusted	0.03	0.1	0.3	1	3	10	16	33	50

Blistering Degree (ASTM D 714)

frequency	dense, D	medium dense, MD	medium, M	few, F
size	10	8	6, 4	2
comments	no blistering	smaller size blister easily seen by unaided eye	progressively larger sizes	

paint with CaTPP. Except for the epoxy coatings (paints 2 and 4), the rest of the tested paints exhibited blisters of different sizes and surface density, after 700 h of exposure. Paint 4 developed blisters after 1200 h of exposure.

The anticorrosive behavior of these pigments in the salt spray chamber must be compared with a pigment of the same sort, that is to say aluminum tripolyphosphate (AlTPP), and with their predecessor, zinc phosphate. The anticorrosive performance of aluminum tripolyphosphate is poor due to its high acidity[29] and failed in all tests, accelerated as well as electrochemical ones; however, its anticorrosive performance was improved by carefully selecting the complementary pigments.[14,29] In this sense ZnTPP and CaTPF displayed much better protective properties than AlTPP.

The comparison between CaTPP and ZnTPP and their predecessor, zinc phosphate, is rather complicated because there are several products in the market, each one of different quality.[28] Alkyd paints formulated with a good product allowed good results to be obtained in the salt spray test after 1000 h of exposure (qualification 8); this behavior was impaired as time elapsed (qualification 6 after 1700 h of exposure).[28] As it could be seen from results displayed in Table 4, alkyd paints of similar composition but pigmented with Ca and ZnTPP showed a better anticorrosive performance. Epoxy paints formulated with zinc phosphate began to fail after 1700 h of exposure in the salt spray test[28] while similar paints formulated with Ca and ZnTPP underwent 2400 h of exposure, maintaining an acceptable degree of protection.[16]

The values reported in Table 5 point out that adhesion forces at the alkyd paint/metal interface began to fall down after 24 h of exposure and were totally lost after 380 h in the salt spray cabinet. However, the substrate remained protected beyond 1200 h of exposure, thus demonstrating the anticorrosive properties of tripolyphosphates. Epoxy paints did not show changes in adhesion values during the first 380 h of exposure.

The anticorrosive behavior of water-borne paints formulated with CaTPP (paints 5 and 6) was poorer than those containing ZnTPP (paints 7 and 8). The epoxy paints containing ZnTPP showed an excellent performance after 2400 h of exposure; it was still better than that of solvent-borne paints. Blistering was less severe than in the case of solvent borne paints. Smaller blisters with very low surface density were observed (Table 4). No loss of adhesion was reported during the first day of exposure in the salt spray chamber. An important decrease in the adhesion forces was observed in paint 8 (water-borne epoxy, PVC 25%, containing ZnTPP) which is totally compensated by the inhibitive action of the pigment (Table 5).

Table 5. Average Values of Paint/Steel Adhesion

	hours of exposure		
paint	0	24	380
1	5B	3B	
2	5B	5B	5B
3	5B	4B	
4	5B	5B	5B
5	5B	5B	4B
6	5B	5B	5B
7	5B	5B	5B
8	5B	5B	2B

Tape-Test Method B (ASTM D 3359/97)

classification	5B	4B	3B	2B	1B	0B
removed area/%	0	<5	5−15	15−35	35−65	>65

Table 6. Rusting and Blistering Degrees of Painted Panels after the Humidity Chamber

	hours of exposure			
	400		900	
paint	rusting	blistering	rusting	blistering
1	8	6MD	6	4D
2	10	8F	10	8F
3	7	4MD		
4	10	10	10	10
5	10	8M	10	8M
6	10	6M	9	6MD
7	10	4D	8	2D
8	10	6D	8	2D

Almost all painted panels developed blisters of very different size and surface density when exposed to the humidity chamber (Table 6). The only exception is paint 4, a solvent-borne epoxy containing ZnTPP which did not blister in the whole test period. There are several cases in which no sign of corrosion was detected in spite of blistering development, and this may be attributed to the inhibitive action of the tripolyphosphates.

Alkyd paints formulated with zinc phosphate blistered after 350 h in the humidity chamber, as alkyd paints formulated with CaTPP and ZnTPP did. Epoxy paints formulated with zinc phosphate were more resistant to blistering than alkyd coatings, although, finally, blistering begun, in all cases, after 750 h of exposure. However, epoxy paints formulated with Ca and

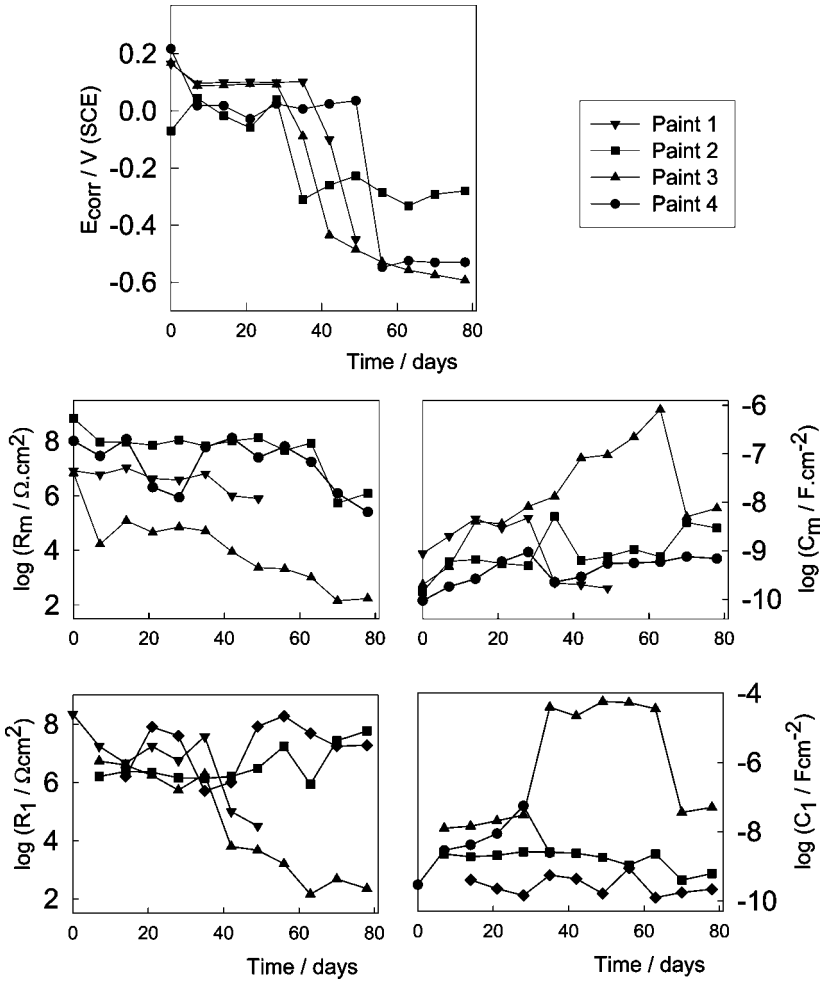

Figure 6. Time dependence of the different parameters characterizing the electrochemical behavior of steel coated with solvent-borne coatings pigmented with calcium tripolyphosphate and zinc tripolyphosphate. Electrolyte: 0.5 M NaCl.

ZnTPP seemed to be a little more resistant to blistering; for instance, paints formulated with ZnTPP did not blister up to 900 h of exposure. Paints pigmented with CaTPP developed some blisters on their surface after 400 h of exposure, but they did not propagate as time went on, as it occurred with similar paints containing zinc phosphate.[16]

Performance of Anticorrosive Paints in Electrochemical Tests. Solvent borne paints (alkyd and epoxy) pigmented with CaTPP displaced E_{corr} toward typical values corresponding to passivated steel. The protection afforded by the alkyd paint (paint 1) was lost after 30−35 days of immersion while the E_{corr} of steel coated with the epoxy paint diminished markedly after 30 days of exposure and remained oscillating around −0.300 V during the rest of the test period (Figure 6).

ZnTPP also displaced steel corrosion potential toward more noble values. Positive values were observed after the first day of exposure, and they were maintained at least during the first three weeks of immersion, thus indicating full protection of the steel substrate. E_{corr} of steel coated with the alkyd paint evolved to characteristic values of painted steel undergoing corrosion, after 30 days of exposure. The same could be observed with the epoxy paint but after 50 days of immersion. It must be pointed out that alkyd paints showed an interesting behavior in the sense that the corrosion potential of coated steel remained quite positive beyond three weeks of immersion (Figure 6). Normally, similar paints, formulated with zinc phosphate, failed in this test after the first few days of immersion, and the E_{corr} rapidly moved toward typical values of corroding painted steel.[15–17,23]

The anticorrosive performance of water-borne paints pigmented with CaTPP was poor (Figure 7) because E_{corr} decayed to negative values after the first week of immersion. This is not usual in the case of epoxy resins which are resistant to immersion; therefore, this points to some incompatibility between CaTPP and the resin. It will be seen later that the barrier effect was also lost with concomitant changes in the film dielectric capacitance.

On the other hand, water-borne paints containing ZnTPP showed a very good anticorrosive performance; E_{corr} was displaced toward a more positive value for a long time, 70 days for the paint with the lowest PVC value and 25 days for the other paint. However, this last paint showed an excellent capacity to recover the passive condition up to 50 days of immersion which was attributed to the inhibitive action of the pigment. It must be noted that the paint with the lowest PVC value showed a better anticorrosive performance than the solvent-borne paint which had similar formulation features.

Equivalent Circuits. Impedance spectra give useful information concerning the evolution of both the organic coating protective properties and the kinetics of the underlying steel corrosion process as a function of the immersion time in the selected electrolyte. Many processes such as the dynamic nature of the membrane barrier effect, the pigment anticorrosive action,

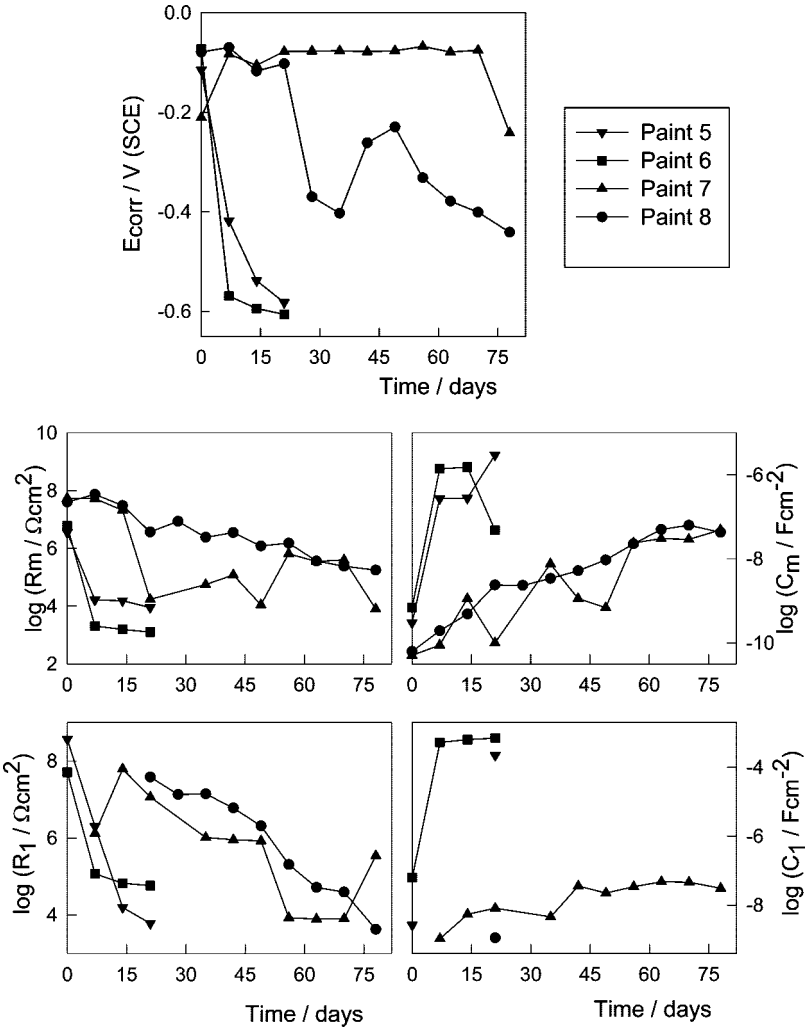

Figure 7. Time dependence of the different parameters characterizing the electrochemical behavior of steel coated with water-borne coatings pigmented with calcium tripolyphosphate and zinc tripolyphosphate. Electrolyte: 0.5 M NaCl.

changes in the disbonded area, and so forth are responsible of the variations of the coated steel/electrolyte impedance. The point of view adopted in this paper was that of Amirudin and Thierry[31] 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. Fortunately, appropriate equivalent circuits have been proposed to describe the behavior of painted metals (Figure 8); these circuits were discussed previously by several authors.[32–46] Experimental impedance data are usually fitted with nonlinear least-squares algorithms, involving the transfer function derived from the equivalent circuit models, to obtain circuit parameters.[27,31–35,40] The impedance of a high-quality, nondefective organic coating is that of a dielectric capacitor with a frequency dependence expressed by the following equation:

$$Zc = -j/wC$$

However, as the coating degrades, an in-phase component develops as a result of shorting the organic coating capacitance with a parallel resistor. This resistor represents the development of ionic conducting paths which may occur through microscopic pores or virtual pores defined by low cross-linking regions in the polymer with concomitant high ionic transport. This model has essentially been proposed by Kendig and Scully,[37] Brasher and Nurse,[40] Leidheiser and Kendig,[41,42] Mansfeld and Kendig,[43] and Beaunier et al.[44] Thus, Rs represents the electrolyte resistance between the reference and working (coated steel)

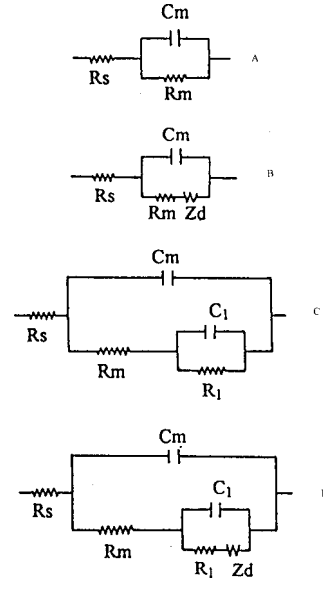

Figure 8. Equivalent circuits to fit experimental electrochemical impedance spectra.

electrodes, R1 the resistance to the ionic flux through paths short-circuiting the paint film, and C1 the dielectric capacitance of the intact part of the same film (Figure 8A). Once the permeating and corrosion-inducing chemicals (water, oxygen, and ionic species) reach the electrochemically active areas of the substrate, particularly the bottom of the paint film pores, metallic corrosion takes place, and its associated parameters, the double layer capacitance (C2) and the charge transfer resistance (R2), can be obtained from the fitting procedure. It is important to remark that R2 and C2 values vary inversely and directly, respectively, and with the size of the attacked metallic area. There is almost a unique opinion that a polymer coated metal is represented by the circuit in Figure 8C when water penetrates the coating and reaches the metal. It is also agreed that the general impedance may include the Zd, the mass transfer (Warburg) impedance.[31] Sometimes, when the strength of the bonding forces at the paint/substrate interface are affected (e.g., by wet adhesion), facilitating lateral diffusion of the electrolyte, other processes under and/or within the intact parts of the coating could be graphically and/or numerically separated,[45] causing the appearance of additional time constants (R3C3). Distortions observed in these resistive−capacitive contributions indicate a deviation from the theoretical models due to either lateral penetration of the electrolyte at the steel/paint interface (usually started at the base of intrinsic or artificial coating defects), underlying steel surface heterogeneity (topological, chemical composition, surface energy), and/or difusional processes that could take place along the test.[46–48] Since all these factors cause the impedance/frequency relationship to be nonlinear, they are taken into consideration by replacing the capacitive components (Ci) of the equivalent circuit transfer function by the corresponding constant phase element Qi (CPE), thus obtaining a better fit of data.[27,31] The CPE is defined by the following equation:[49]

$$Z = \frac{(j\omega)^{-n}}{Y_0} \tag{1}$$

where Z is the impedance of the CPE ($Z = Z' + Z''$; Ω), j is the imaginary number ($j^2 = -1$), ω is angular frequency (rad), n is CPE power ($n = \alpha/(\pi/2)$, dimensionless), α is the constant phase angle of the CPE (rad), and Y_0 is part of the CPE independent of the frequency (Ω^{-1}).

The accuracy of the fitting procedure was measured by the χ^2 parameter obtained from the difference between experimental and fitted data; the most probable circuit was selected providing that $\chi^2 < 10^{-4}$. In the present work, the fitting process was mainly performed using the phase constant element Qi instead of the dielectric capacitance Ci. However, this last parameter was used in the plots to facilitate results visualization and interpretation.

The relative performance of painted steel samples, submerged in 0.5 M NaCl solution, was evaluated by analyzing the variation of Ri and Ci with the exposure time (Figures 6 and 7).

Alkyd paints showed an initial Rm value close to 10^7 Ω·cm^2 (Figure 6), which is indicative of the presence of a good barrier effect.[38] The initial barrier effect afforded by the paint formulated with CaTPP (paint 1) lasted at least 40 days, but it was lost within the first week of immersion in the case of the paint pigmented with ZnTPP (paint 3). However, it maintained a rather high value, close to 10^5 Ω·cm^2, for more than 1 month. The anticorrosive protection provided by the paint formulated with ZnTPP relyed mostly on the pigment while, in the other case, a considerable barrier effect must be taken into account to explain the anticorrosive action of the coating. It is thought that the acidic proton generated by hydrolysis of the tripolyphosphate anion could restrain the degradation process of alkyds under immersion by reacting with hydroxyl ions coming from the curing process of the resin.

The capacitance of alkyd paint 1, pigmented with CaTPP, increased during one month to finally decay to a value denoting protection of the susbstrate. The capacitance of paint 3 increased continuously during the immersion period, thus indicating the continuous deterioration of the coating, although a recovery was observed at the end of the test period, probably due to pore blocking by corrosion products (Figure 6).

The ionic resistance of solvent-borne epoxy paints was found to be high, as it could be expected from this type of resin. The observed values fluctuated between 10^6 and 10^8 Ω·cm^2, during 70 days, thus indicating strong barrier properties of the paint film. Cm of epoxy paints was found to fluctuate around 10^{-9} F·cm^{-2} (Figure 6), this value being characteristic of no damaged organic coatings.[38,50,51]

The different behaviors of both types of coatings could be also appreciated following the variation of the parameters corresponding to the relaxation of the faradaic process. R_1 of alkyds was high during a certain period of time and, then, decreased to very low values. On the other hand, R_1 for epoxy paints was higher than 10^6 Ω cm^2, and C_1 maintained very low values during the whole test period.

Paints formulated with CaTPP and the water-borne resin (paints 5 and 6) failed prematurely, as it was said previously, and the barrier properties were lost within the first few days of immersion; concomitantly Cm increased (Figure 7). Other electrochemical parameters such as R_1 reached low values, for both coatings, after two weeks of immersion, and as a consequence of this deterioration process, C_1 exhibited higher values.

The water borne paints containing ZnTPP and two different PVC values (paints 7 and 8) showed similar behavior in this test (Figure 7). They possessed a high barrier effect at the beginning of the exposure period ($R_m \sim 10^8$ Ω·cm^2) which declined along 2 months of immersion to achieve a value close to 10^6 Ω·cm^2 at the end of the immersion period. This means that the paints maintained relatively good barrier properties all along the exposure time. The paint with a PVC value of 20% exhibited an oscillating behavior due to pore opening followed by blocking with reaction products. The value of Cm for both paints was characteristic of non-deteriorated coatings, at least during the first two weeks of immersion. Then, Cm values increased slowly with time as the ionic resistance decreased in the same way. The charge transfer resistance also varied similarly to the ionic resistance of coated steel, exhibiting a decreasing tendency. The paint with the lowest PVC value showed a certain recovery of this parameter after 70 days of immersion, probably due to the accumulation of a greater amount of corrosion products at the bottom of the paint defects.

Performance of Anticorrosive Paints in Natural Weathering Tests. As it could be seen from Table 7, all paints showed an acceptable anticorrosive behavior during the first five years of exposure to the selected environment. The exceptions were the water-borne paints with the higher PVC value, which failed after 4 years of exposure.

After 7 years of natural weathering, all solvent-borne paints exhibited good anticorrosive behavior showing that the epoxy paints had a slightly better performance. It is important to point out that, in all cases, the failure was due to corrosion and that

Table 7. Rusting Degree of Painted Panels after the Natural Weathering Test

	years of exposure			
paint	4	5	6	7
1	10	10[a]		
2	10	10	10	10
3	10	10	8	8
4	10	10	10	9
5	9	7		
6	6			
7	10	8		
8	6			

[a] Failed after 5 and a half years (6).

no blistering was detected even after 4 (water-borne paints) or 7 years of exposure (solvent-borne paints).

Conclusions

1. Calcium and zinc tripolyphosphates, both pigments, inhibit corrosion in aggressive media as it could be deduced from the reduction of steel corrosion rate in pigment suspensions compared with the value obtained in the supporting electrolyte.

2. The solubility of calcium tripolyphosphate and zinc tripolyphosphate is relatively high, compared with that of orthophosphates; this implies a higher concentration of the passivating species in the pore solution. However, the values reported for the solubility of the pigment are adequate to formulate an anticorrosive coating.

3. Electrochemical tests in pigment suspensions may be useful to predict the ability of this kind of substance to function as inhibitors in organic coatings. In this sense corrosion rate is a useful parameter to be taken into account because the anticorrosive performance of paints may depend on it, as it occurred with water-borne paints.

4. It is also possible to formulate water-borne epoxy paints with excellent performance, employing zinc tripolyphosphates as anticorrosive pigment. More than 2400 hs of exposure in the salt spray test are to be expected for this pigment.

5. For solvent and water-borne paints, the recommended anticorrosive pigment concentration is 30% of the total pigment content.

6. The corrosion potential of painted steel panels also demonstrated the beneficial effect of tripolyphosphates in restraining corrosion of the base metal. Corrossion potential of panels coated with solvent-borne paints was displaced to more positive values with respect to values reported for coated steel undergoing corrosion. This displacement was maintained, at least, during one month and was also observed for water-borne paints formulated with zinc tripolyphosphate.

7. EIS tests performed on painted panels revealed that the substrate was protected, in a first stage, by a barrier effect, and when this barrier effect diminished, the inhibitive action of the pigment was observed, as it could be deduced from the values of the charge transfer resistance.

8. Results in the long term test are encouraging. The solvent-borne paints, principally epoxy paints, had a good performance after 7 years of exposure.

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