

Calcium Tripolyphosphate: An Anticorrosive Pigment for Paint

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INTRODUCTION

The use of chromium and lead-based compounds as anticorrosive pigments is being restricted due to their negative impact on the environment and human health. Legal restrictions imposed on their use in paint technology have challenged the paint industry and research laboratories to look for adequate replacements. The new pigment must not only be as good as the classical ones, but must do so at a similar production cost, that is to say “better paints at the same price.”

Zinc phosphate pigments and related compounds are gradually replacing the classical anticorrosive pigments. Studies of the anticorrosive performance of zinc phosphate have led to contradictory results and are not yet conclusive. Its behavior could be improved by controlled chemical modification or by changing the anion orthophosphate to the tripolyphosphate one.¹⁻⁸ Calcium acid phosphate has been found to give better anticorrosive performance than zinc phosphate.^{9,10}

Phosphates were replaced by tripolyphosphates in order to meet the demands of high technology applications such as coil coatings. Although calcium tripolyphosphate was known for its anticorrosive properties,¹¹ which were due to the high charge of the salt, aluminum tripolyphosphate was preferred for the preparation of anticorrosive paints.^{3,12-15}

The aim of this study was to evaluate the anticorrosive properties of calcium tripolyphosphate. The pigment was obtained in the laboratory through precipitation from soluble salts of the anion and the cation, respectively.^{16,17} The physico-chemical characteristics of the pigment, as well as the inhibitive properties, were determined by different techniques. Another series of studies involved the preparation of several paints employing either an alkyd resin or an epoxy one with different anticorrosive pigment concentrations. Painted panels were subjected to accelerated and electrochemical tests.



The objective of this work was to evaluate the performance of calcium tripolyphosphate in anticorrosive paints. Its anticorrosive properties were studied in pigment suspensions and in solventborne paints with 10% and 30% of the pigment by volume and a pigment volume concentration/critical pigment volume concentration (PVC/CPVC) equal to 0.8. The behavior of paints formulated with epoxy and alkyd resins was assessed by accelerated (salt spray cabinet and humidity chamber) and electrochemical tests (corrosion potential, ionic resistance, and polarization resistance).

Calcium tripolyphosphate was proven to inhibit steel corrosion when incorporated in a paint film. Good protection was achieved employing only 10% by volume of the pigment, instead of 30%, as was suggested in the case of phosphates. The anti-corrosion protection afforded by alkyd paints was impaired when the pigment content was increased. Epoxy paints seemed to be less sensitive to the pigment content.

EXPERIMENTAL

Pigment Preparation and Characterization

Calcium tripolyphosphate was prepared by mixing an acid solution of sodium tripolyphosphate and an acid

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Table 1—Paint Composition (% Volume of Solids)

Paint	1	2	3	4	5	6
Anticorrosive pigment	3.3	9.8	3.3	9.8	3.3	9.8
Titanium dioxide (TiO ₂)	6.3	4.7	6.3	4.7	6.3	4.7
Barium sulphate (BaSO ₄)	16.4	11.9	16.4	11.9	16.4	11.9
Talc (3MgO.4SiO ₂ .H ₂ O)	7.0	6.6	—	—	7.0	6.6
Zinc oxide (ZnO)	—	—	7.0	6.6	—	—
Alkyd resin	67.0	67.0	67.0	67.0	—	—
Epoxy resin/ Polyamide resin (1/1 ratio) ...	—	—	—	—	67.0	67.0
Anticorrosive pigment/ total pigment (v/v)	10	30	10	30	10	30

Table 2—Physical and Chemical Properties of Calcium Tripolyphosphate

Solid			Aqueous Extract			
Composition (% p/p)		Density (g/cm³)	Solubility (ppm)		Conductivity (µS)	pH
Ca²⁺ 22.3	PO₄³⁻ 69.7	2.11	Ca²⁺ 12.6	PO₄³⁻ 435	412	5.48

solution of calcium nitrate and adjusting the final pH to 6-8 with 20% sodium hydroxide solution. The precipitate was allowed to settle for 24 hr, was filtered, and was then dried at room temperature (23±3°C) with the aid of a flow of air. The pigment was washed twice with distilled water and dried in the same way.*

The physico-chemical properties of calcium tripolyphosphate that were obtained in the laboratory, such as density, pH, and conductivity of saturated aqueous solution, and the solubility product constant (K_{sp}) were determined.

Evaluation of the Inhibitive Properties of Pigment Suspensions

The inhibitive properties of the pigment were evaluated by measuring the corrosion potential of an AISI 1010 steel

*The preparation and employment of calcium tripolyphosphate as anticorrosive pigment is being protected by an Argentine patent, now under examination.

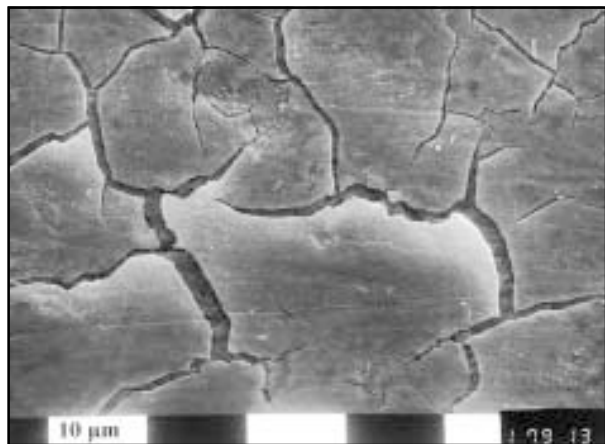


Figure 1—SEM micrograph of the film formed on the steel panel in contact with pigment aqueous suspension (3500X).

electrode in a pigment suspension after 24 hr exposure. The saturated calomel electrode (SCE) was used as reference and the electrolyte was a 0.025 M sodium perchlorate solution.

Steel polarization resistance in the same pigment suspensions was also measured in comparison with bare steel, with and without

IR-drop compensation. The reference electrode was SCE and the counterelectrode was a platinum grid. The sweep amplitude was ±20 mV, starting from the corrosion potential at a scan rate of 0.166 mV/s. Measurements were taken employing model 273A EG&G PAR Potentiostat/Galvanostat plus SOFTCORR 352 software.

The protective layer formed after 24 hr exposure to the pigment suspension was examined by scanning electron microscopy (SEM). The surface amount of iron, phosphate, and calcium was determined by energy dispersive X-ray analysis (EDXA).

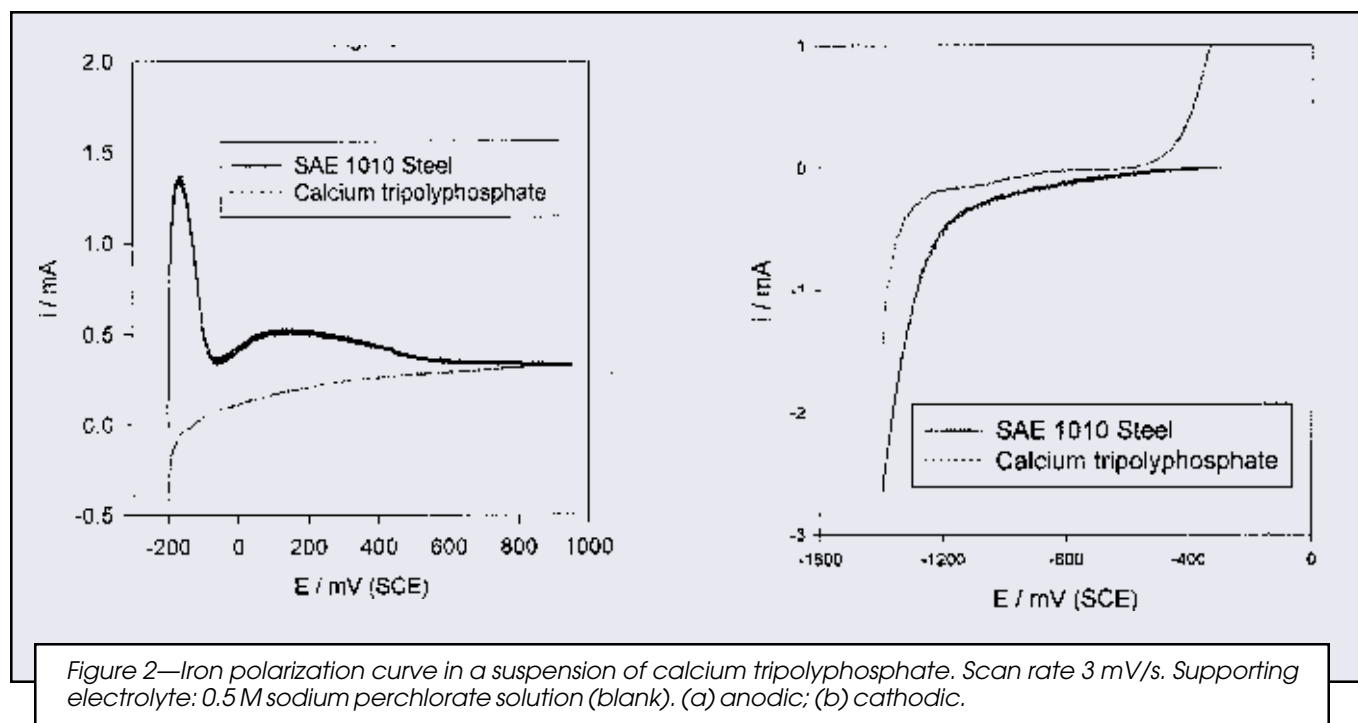
Anodic and cathodic polarization curves of an iron electrode in pigment suspensions in 0.5 M sodium perchlorate solution were also obtained after 24 hr exposure. The cell employed to carry out these measurements was that employed to determine the polarization resistance. The sweep began in the vicinity of corrosion potential, at a scan rate of 3 mVs⁻¹.

Paints Composition, Manufacture, and Application

The materials used to form the films were as follows: a medium oil alkyd (50% linseed oil, 30% o-phthalic anhydride, 8% pentaerythritol and glycerol, and 12% pentaerythritol resinate) and an epoxy-polyamide resin.

The solvent mixtures employed were white spirit for the alkyd paints and xylene/methyl isobutyl ketone/butoxyethanol (13/45/42% by weight) for the epoxy paints.

Two different contents of calcium tripolyphosphate were employed, 10% and 30% by volume, with respect to the total pigment concentration. Titanium dioxide, barium sulfate, and talc or zinc oxide were incorporated to complete the pigment formula. It was decided to test the effect of replacing talc with zinc oxide in alkyd paints to avoid a possible leaching of soluble species by pigment-binder interaction, which may be strong in the case of the anion tripolyphosphate and the acid groups of the binder.



Pigments were dispersed in the vehicle employing a ball mill with a 3.3 L jar for 24 hr to achieve an acceptable dispersion degree.¹⁸ The PVC/CPVC ratio was 0.8. Composition of tested paints is shown in Table 1.

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 means of a brush up to a thickness of 75±5 µm. Painted panels were kept indoors (20±2°C, 65% RH), for seven days before being tested.

Performance of Anticorrosive Paints Through Accelerated and Electrochemical Tests

A set of three panels was placed in the salt spray chamber (ASTM B 117). A scratch line was made through the coating on each panel with a sharp instrument (ASTM D 1654), so as to expose the underlying metal to the aggressive environment. Rusting (ASTM D 610) and blistering (ASTM D 714) degrees and the failure at the scratch mark (ASTM D 1654) were evaluated after 700 and 1000 hr of exposure. The adhesion of the coatings to steel was measured by the tape pull test (ASTM D 3359) after 72, 170, and 700 hr exposure to the salt spray chamber and then compared with the value obtained before performing the test.

Another set of panels was placed in the humidity chamber at 38±1°C for 3600 hr (ASTM D 2247). The blistering (ASTM D 714) and the rusting (ASTM D 610) degrees were evaluated periodically.

The electrochemical cells used to measure the corrosion potential were constructed by delimiting 3 cm² circular zones on the painted surface by placing an acrylic tube, 7.0 cm high, on the painted specimen and filling it with the support-

ing electrolyte (0.5 M sodium perchlorate solution). The reference electrode was an SCE and measurements were taken with a high impedance voltmeter.

The resistance between the coated steel substrate and a platinum electrode was also measured employing the above described cells and an ATI Orion model 170 conductivity meter at a 1000 Hz frequency.

The polarization resistance of painted specimens was determined as a function of immersion time by employing the cell described previously and a platinum grid as the counterelectrode. The voltage scan was ±20 mV, starting from the corrosion potential at a scan rate of 0.166 mV/s. Measurements were taken employing a Model 273A EG&G PAR Potentiostat/Galvanostat plus SOFTCORR 352 software.

RESULTS AND DISCUSSION

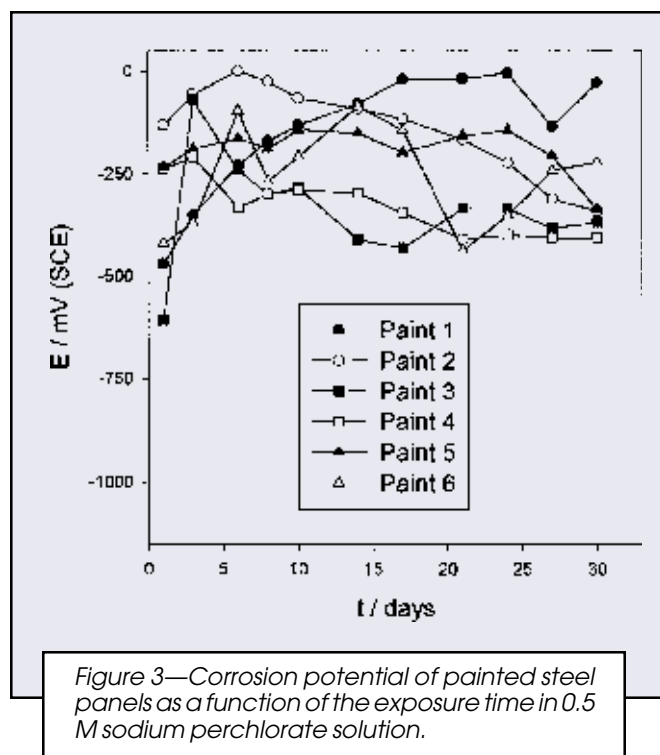
Pigment Characterization

As stated previously, calcium triphosphate could be prepared from soluble salts of the cation and the anion, respectively, if the pH of the pigment suspension is 5.48 (see Table 2); above this pH value, the pigment precipitated

Table 3—Corrosion Potential and Polarization Resistance (with and without IR-drop Compensation) of SAE 1010 Steel in Calcium Triphosphate Suspensions

	Potential (mV)	R _{pc} ^a (kΩ·cm ⁻²)	R _p ^b (kΩ·cm ⁻²)	(R _{pc}) _{pigment} / (R _p) _{Blank}
Calcium triphosphate	-623	2.7	4.9	19.6
Blank (SAE 1010 steel)	-635	0.33	0.25	1.0

(a) R_{pc}—Polarization resistance with IR drop compensation
(b) R_p—Polarization resistance without IR drop compensation



quantitatively. The pigment mole ratio, $\text{Ca(II)}/\text{P}_3\text{O}_{10}^{5-}$, was found to be equal to 2.09. It was obtained determining, experimentally, the amount of calcium linked with the tripolyphosphate anion by employing conventional analytical techniques. Thus, in accordance with this result, the stoichiometry of the obtained product was $\text{Ca}_2\text{MP}_3\text{O}_{10}$ ($\text{M}=\text{H}$ or Na). The K_{sp} was 5.0×10^{-20} as calculated from the precipitation curve of the pigment in question. The K_{sp} of calcium tripolyphosphate was higher than that of zinc phosphate (9.1×10^{-33}). As a consequence, the saturated solution of the tripolyphosphate has a higher phosphate concentration (Table 2; 435 ppm) than the corresponding zinc phosphate saturated solution (less than 1.5 ppm¹⁹). The higher content of phosphate was thought to be useful to achieve a better passivation of the steel substrate. Due to the relatively low pH of the pigment suspension and taking into account possible interactions with acid binders, zinc oxide was used as complementary pigment in some formulations to partially neutralize the acidity of the medium.

Table 4—Rusting (ASTM D 610) and Blistering Degrees (ASTM D 714) and Failure at the Scribe (ASTM D 1654) of the Painted Panels in the Salt Spray Chamber (ASTM B 117)

Paints	Time (hr)					
	700			1000		
	Rust	Blistering	Scribe	Rust	Blistering	Scribe
1	10	10	10	8	— ^a	— ^a
2	9	4F	10	6	— ^a	— ^a
3	10	10	10	10	10	9
4	9	4F	9	8	4F	9
5	8	6MD	9	8	4MD	8
6	9	10	9	9	7F	9

(a) Specimens exhibited serious adhesion failure.

Electrochemical tests performed employing pigment suspensions showed that calcium tripolyphosphate prevented steel corrosion. Although the corrosion potential of SAE 1010 steel in the pigment suspension was not very different from that of steel in the supporting electrolyte (blank), the polarization resistance was strikingly higher (19 times) indicating that corrosion was restrained by the pigment (Table 3).

The presence of a protective layer on steel panels brought in contact with the pigment suspension was detected by SEM (Figure 1). The protective film appeared to be non-expansive iron oxide stabilized by the presence of the tripolyphosphate anion and had two layers. The composition of the external layer, obtained by EDXA, was 81% of Fe, 16% of P, and 3% of CaO (average values), while the internal one contained 90% Fe, 9% P, and 1% Ca. The phosphate content, either in the external film or in the internal layer, was higher than in the films obtained when zinc phosphate was used as anticorrosive pigment.²⁰ The external layer, with a higher phosphate content, was found to be more compact than the internal one. Sometimes, small particles of iron oxide appeared along the cracked surface of the protective film, probably blocking the pores of the film through which oxidation can take place after water and oxygen permeation.^{21,22}

The anodic polarization curve (Figure 2a) shows that the steel was passivated by the presence of the pigment. The oxygen reduction current diminished notably; it was almost six times smaller than the corresponding value of the blank (Figure 2b). So, a substantial reduction of the steel corrosion rate may be expected due to the formation of the protective film described previously.

These preliminary studies confirmed the inhibitive properties of calcium tripolyphosphate and encouraged its use in anticorrosive paints.

Performance of Anticorrosive Paints in Accelerated Tests

The results obtained in the salt spray test, which represents a very aggressive environment, showed that paints pigmented with calcium tripolyphosphate had good anticorrosive behavior. In the case of alkyd paints, the best performance was achieved employing 10% by volume of the pigment calcium tripolyphosphate with zinc oxide as the complementary pigment. The presence of zinc oxide also helped to improve the performance of the alkyd paint with 30% v/v of the anticorrosive pigment, after 1000 hr exposure. These results suggested that the paints with the lower pigment content had better anticorrosive performance. As an example, paint 2, alkyd resin with 30% of anticorrosive pigment and talc, obtained a qualification of 6 after 1000 hr exposure while the qualification for paint 1 with 10% of calcium tripolyphosphate was 8 (Table 4). The failure of paint 2 was attributed to the higher pigment content in combination with the less resistant alkyd resin. This paint, as it will be shown later, had one of the lower ionic resistance values. It was thought

Table 5—Coating Adhesion (ASTM D 3359) after Exposure to the Salt Spray Chamber

TPaint	Time (hr)			
	0	72	170	720
1	5B	3B	0B	— ^b
2	5B	1B	— ^b	— ^b
3	5B	5B	5B	4B
4	5B	5B ^a	5B ^a	— ^b
5	5B	5B	5B	5B
6	5B	5B	5B	5B

(a) Specimens with cohesive failure within the paint film.
(b) Specimens exhibited serious adhesion failure.

that the higher permeability of the coating was due to the relatively high solubility of the pigment enhanced by acid-base interaction with the binder.

Epoxy paints also had good anticorrosive performance and seemed not to be largely affected by the pigment content. The binder appeared to be more tolerant of the acid-base characteristics of the pigment. Paints with the highest anticorrosive pigment showed a slightly better behavior.

The anticorrosive behavior of alkyd paints pigmented with 10% v/v of calcium tripolyphosphate was equal to that of paints containing zinc phosphate and showed a better performance when zinc oxide was incorporated into the pigment formula. No significant differences were encountered when the epoxy paints were compared.¹⁹

Alkyd paints containing calcium tripolyphosphate performed better than similar paints containing commercial aluminum tripolyphosphate pigments. When the binder contained an epoxy resin, the anticorrosive behavior was dependant on the type of commercial aluminum tripolyphosphate employed in the paint's formulation. The anticorrosive behavior may have been similar or superior when calcium tripolyphosphate was employed.²³

In contrast with the paints containing zinc phosphate,¹⁹ all tested paints, except paint 3, developed blisters. After 700 hr testing, blistering was noticed in the paints with the highest anticorrosive pigment content and formulated with the alkyd resin. After 1000 hr exposure, the paint film exhibited serious adhesion problems when talc was used as the complementary pigment and the panels were taken out of the salt spray cabinet. The presence of zinc oxide in the paint film improved blistering resistance, especially when the anticorrosive pigment content was 10% v/v. In the case of epoxy paints, blistering diminished when the anticorrosive pigment increased.

Little failure at the scribe was detected after 700 hr exposure except for the epoxy paint with 10% v/v of the pigment. The presence of zinc oxide in the pigment formula prevented failure at the scribe in alkyd paints until 1000 hr exposure.

The adhesion of the alkyd paints after exposure to the salt spray test was affected by the presence of talc in the pigment formula, showing an important decrease after 72 hr exposure, particularly for the highest anticorro-

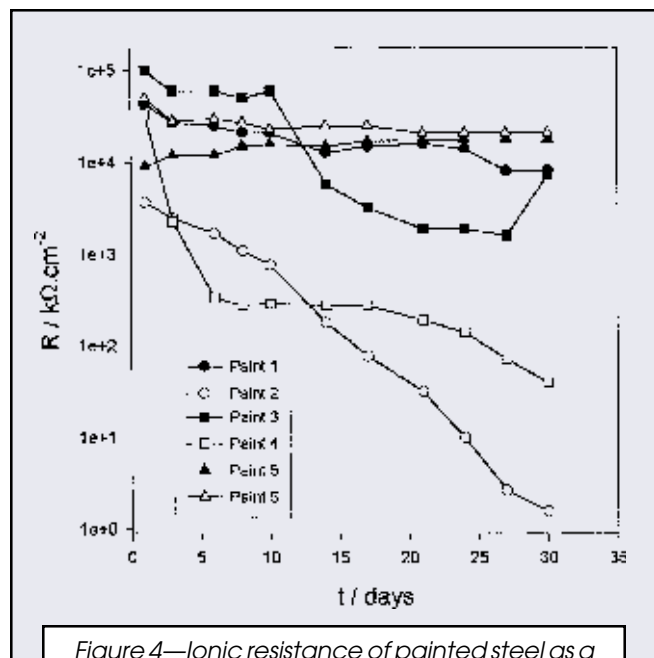


Figure 4—Ionic resistance of painted steel as a function of the exposure time in 0.5 M sodium perchlorate solution.

sive pigment content (Table 5). The replacement of talc by zinc oxide in alkyd paints led to good results after 700 hr exposure when the pigment content was 10% v/v. No adhesion loss was detected in the case of epoxy paints at the end of the test.

Alkyd paints blistered after 72 hr in the humidity chamber and the blistering degree did not change up to 480 hr; by this time, signs of corrosion appeared on the painted surface (Table 6). Although paints containing zinc oxide had better anticorrosive performance, blisters appeared to be of bigger size; this was attributed to the higher affinity of zinc oxide for water molecules. The anticorrosive behavior and blistering resistance of epoxy paints was clearly superior to alkyd ones in that they underwent 3600 hr of exposure with a qualification of 10 and little blistering in the case of paint 6.

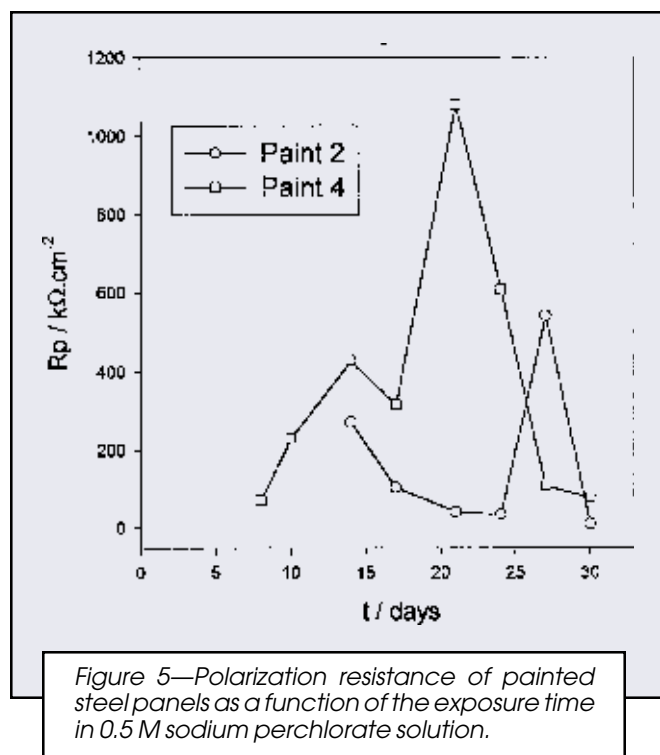
Performance of Anticorrosive Paints in Electrochemical Tests

The measurement of corrosion potential of painted steel as a function of time revealed that calcium tripolyphos-

Table 6—Rusting (ASTM D 610) and Blistering Degrees (ASTM D 714) of Painted Panels Exposed to the Humidity Chamber (ASTM D 2247)

Paint	Time (hr)					
	72		480		3600	
	Rust	Blistering	Rust	Blistering	Rust	Blistering
1	10	8MD	8	8MD	— ^a	— ^a
2	10	6MD	8	6MD	— ^a	— ^a
3	10	6D	9	6D	— ^a	— ^a
4	10	6D	9	6D	— ^a	— ^a
5	10	10	10	10	10	10
6	10	10	10	8F	10	8F

(a) Specimens were taken out of the humidity chamber due to an important blistering and to the onset of corrosion.



phate inhibited corrosion in the sense that the potential remained more positive than the corrosion potential of bare steel (~ -750 mV vs SCE). The corrosion potential of the different paints was, as an average, above -500 mV against SCE (Figure 3). In the case of alkyd paints, the better anticorrosive performance was observed for the lowest anticorrosive pigment content. As pointed out previously, this fact may be due to the relatively high solubility of the calcium tripolyphosphate. Epoxy paints are less sensitive to the pigment content and both paints had similar behavior. In many cases, corrosion potential fluctuated slightly suggesting a certain repassivation of the steel surface.

Corrosion potential measurements indicated that calcium tripolyphosphate showed a better anticorrosive efficiency than zinc phosphate and aluminum tripolyphosphate.^{19,23}

The measured values of the ionic resistance indicated that there was not an important barrier effect in any of the tested paints. The ionic resistance showed little variation during the test period except for the alkyd paints containing 30% v/v of calcium tripolyphosphate. In this last case, ionic resistance diminished quickly, as time elapsed, showing an important deterioration of the paint film. The increased permeability led to poor results in the accelerated tests.

The polarization resistance was not determined in most of the paints studied in this research, due to the high values of the ionic resistance. In these cases a linear response would be obtained indicating an ohmic control of the corrosion process. When the ohmic control disappeared (alkyd paints with 30% v/v of pigment), after the first week of immersion, polarization resistance was measured and resulted higher than the ionic one; thus indicating the inhibitive effect of calcium tripolyphosphate.²⁴ The polarization resistance also depended on the type of comple-

mentary pigment, being higher for zinc oxide than for talc (Figure 5). In this way, the presence of zinc oxide would result in better anticorrosive performance as observed in alkyd paints pigmented with zinc oxide (Table 4).

CONCLUSIONS

The solubility of calcium tripolyphosphate is higher than that of zinc phosphate. This means a higher concentration of the passivating anion in the pore solution which, in turn, resulted in better protection of the steel substrate. Calcium tripolyphosphate inhibited bare steel corrosion by forming an oxide layer of nonexpansive type with a relatively high phosphate content. The inhibitive action of the calcium tripolyphosphate in paints was evidenced in accelerated and electrochemical tests. The corrosion potential was shifted to more positive values (> -500 mV) during the test period. Good anticorrosive performance was achieved when the pigment concentration was 10%, v/v. In the case of alkyd paints, higher contents led to undesirable results. The presence of calcium tripolyphosphate in the film did not generate a significant barrier effect. Increasing the pigment concentration in the alkyd paint led to a deterioration of the paint film. Good correlation was found among accelerated and electrochemical tests.

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