

# Steel Corrosion Protection by Means of Alkyd Paints Pigmented with Calcium Acid Phosphate<sup>†</sup>

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The use of classic anticorrosive pigments is becoming more and more restricted by increasing environmental concerns; they are gradually being replaced by zinc phosphate and related compounds. Other anticorrosive pigments such as surface-exchanged silicas were also proposed. The object of this research is to study the anticorrosive properties of calcium acid phosphate as an inhibitive pigment, introducing a careful selection of complementary pigments in order to achieve an efficient anticorrosive protection. Several alkyd paints were prepared and evaluated through accelerated and electrochemical tests. The nature of the passive film formed was also studied. Paint containing zinc oxide and calcium carbonate (50/50) as complementary pigments showed the best performance in the salt spray test. Zinc oxide and calcium carbonate decreased film permeability and improved steel passivation. The passive film was composed of ferric oxyhydroxide, the pores of which became plugged by ferric phosphate.

## Introduction

The use of classic anticorrosive pigments is being more and more restricted by increasing environmental awareness as well as stringent national and international regulations and directives. This situation takes into account that the use of chromate pigments implies the risk of cancer.

The long-awaited reduction in the usage of classic active pigments has induced a considerable search for suitable alternative products for more than 15 years. Particular attention has been paid to zinc phosphate. In subsequent years, it was found that the effectiveness of zinc phosphate could be improved by controlled chemical modification of its structure with suitable elements or by change of the anion orthophosphate by a polyphosphate one.<sup>1–8</sup>

The comparative anticorrosive performance of calcium acid phosphate and zinc phosphate was established in a previous paper.<sup>9,10</sup>

The aim of this paper is to study the anticorrosive properties of calcium acid phosphate as an inhibitive pigment, introducing an important modification with respect to authors' previous studies.<sup>9,10</sup> This modification is concerned with a careful selection of complementary pigments in order to achieve an efficient anticorrosive protection.

To test the performance of calcium acid phosphate, two different studies were conducted. One series of studies involved the preparation of several paints employing an alkyd resin and different pigment compositions. Painted panels were subjected to accelerated and electrochemical tests. Another series was conducted in order to assess the inhibitive properties of aqueous pigment suspensions by different techniques, studying the properties of the passive layer.

**Table 1. Solids in Paint Composition (Percent by Volume)**

	paint			
	1	2	3	4
calcium acid phosphate	10.0	10.0	10.0	10.0
talc	9.6			
calcium carbonate		9.6		4.8
zinc oxide			9.6	4.8
titanium dioxide	3.8	3.8	3.8	3.8
barium sulfate	9.6	9.6	9.6	9.6
alkyd resin	46.0	46.0	46.0	46.0

## Experimental Section

### Paints Composition and Manufacture. (a) Binder.

The film-forming material was an alkyd resin (50% solution in white spirit). The resin employed in this research had the infrared (IR) spectrum corresponding to an oil-medium alkyd resin. It showed the characteristic peak of alkyds at 1275 cm<sup>-1</sup> and other peaks assigned to the stretching of the C–H bond in an oil (2870 and 2930 cm<sup>-1</sup>), the stretching of the C=C bond (1490, 1580, and 1600 cm<sup>-1</sup>), and the bending of the benzene ring (705 and 745 cm<sup>-1</sup>).<sup>11</sup>

(b) **Pigment.** Calcium acid phosphate was employed as an anticorrosive pigment, and its content was 30 vol % with respect to the total pigment formula.<sup>1</sup> Other pigments such as titanium dioxide, magnesium silicate, calcium carbonate, zinc oxide, and barium sulfate were used as complementary pigments. The pigment volume concentration/critical pigment volume concentration (PVC/CPVC) relationship for all of the paint formulations was 0.8, with this value resulting in a similar free binder content in all cases. Paints solids percentages, expressed as percent by volume, are shown in Table 1.

(c) **Paints Preparation.** This was carried out by employing a ball mill with a 3.3 L jar. The resin solution was added first and pigments were incorporated later. The system was dispersed 24 h to achieve an acceptable dispersion degree.<sup>12</sup>

(d) **Paints Application.** Paints prepared in this way were applied by means of a spray gun on ASTM 1010 steel panels (15.0 × 7.5 × 0.2 cm) up to a thickness of

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<sup>†</sup> The process for pigment elaboration and its employment as an anticorrosive pigment is under Patent P19980101262.

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**Table 2. Rusting Degree (ASTM D 610) Failure at the Scribe (ASTM D 1654) and Blistering (ASTM D 714) after 720 h of Exposure in the Salt Fog Chamber for Steel Panels Coated with the Selected Painting Schemes**

paint	anticorrosive paint			blistering degree painted panel	anticorrosive paint + topcoat: rusting degree	
	rusting degree				painted panel	after paint removal
	painted panel	after paint removal	failure at the scribe			
1	8	5	6	4D	10	10
2	9	6	5	6M	6	6
3	10	9	6	0	10	10
4	10	10	7	8F	10	10

75 ± 5 μm. Tested panels were previously sandblasted to Sa 2<sup>1/2</sup> (SIS 05 59 00) and degreased with toluene. The painted panels were kept in the laboratory for 7 days before testing. Two series of panels were tested: one with the primer alone and the other with a complete paint system (a conventional alkyd enamel was used as a topcoat) up to a film thickness of 125 ± 5 μm.

**Laboratory Tests.** Conventional accelerated salt spray and humidity cabinet tests were performed using painted panels to assess paints' anticorrosive properties. In addition, electrochemical measurements were done on similar panels to elucidate the anticorrosive mechanism of these paints.

The coating barrier properties to water vapor were evaluated to understand the coating behavior during the early stages of the corrosion process.

Finally, the nature of the passive layer was investigated by scanning electron microscopy (SEM), Mössbauer spectroscopy, and FT-IR spectrometry.

**Accelerated Tests. (a) Salt Spray Test (ASTM B 117).** A scratch line was made through the coating with a sharp instrument to expose the underlying metal to the aggressive environment. The panels were periodically observed, without removing the coating, to establish the rusting degree (ASTM D 610) and to assess failure at the scribe (ASTM D 1654). In all cases experiments were carried out in triplicate, determining the mean value of the obtained results.

**(b) Humidity Chamber Test.** Another series of panels coated with the anticorrosive paints alone were placed in the humidity chamber at 38 ± 1 °C for 1600 h (ASTM D 2247). The degrees of rusting and blistering were established according to the ASTM D 610 and ASTM D 714 standard specifications, respectively.

**Electrochemical Measurements. (a) Corrosion Potential.** The electrochemical cells to measure the corrosion potential of painted steel as a function of time were constructed by delimiting 3 cm<sup>2</sup> circular zones on the painted surface. An acrylic tube, with one flat end and 7 cm high, was fixed on the specimen with an epoxy sealer and filled with the electrolyte (a 0.5 M sodium perchlorate solution). The corrosion potential of coated steel was measured against a calomel electrode with a high impedance voltmeter.

**(b) Ionic Resistance.** The resistance between the steel substrate and a platinum electrode was also measured by employing the cells described previously and an ATI Orion, model 170, conductivity meter at a 1000 Hz frequency. Similar measurements were performed on uncoated steel.

**(c) Polarization Resistance.** The polarization resistance of painted panels (working electrode) was determined for specimens whose ionic resistance decreased below 10<sup>5</sup> Ω·cm<sup>-2</sup>, as a function of immersion time, employing an electrochemical cell with three electrodes. The reference electrode was the SCE and the

counter electrode a platinum grid. The voltage swept was ±20 mV, starting from the corrosion potential, at a scan rate of 0.166 mV/s. Measurements were carried out by employing an EG&G PAR potentiostat/galvanostat, model 273A, and the software SOFTCORR 352.

**Water Vapor Transmission.** Water vapor transmission was evaluated according to ASTM D 1653, test method B, by applying the paints on filter paper by immersion (dry film thickness 70 μm). Perm cups consisting of a container made of noncorroding material, impermeable to water and water vapor, and of 25 cm<sup>2</sup> area were employed.

**Nature of the Passive Film.** To investigate the anticorrosive properties of calcium acid phosphate, the corrosion potential of an ASTM 1010 steel electrode was measured against a calomel electrode. The electrolyte was a pigment suspension in 0.1 M sodium perchlorate. The morphology of the passive film formed on the steel surface was studied by scanning electron microscopy and its composition determined by Mössbauer spectroscopy. The final product resulting from the reaction with calcium acid phosphate and iron powder was also identified by means of an FT-IR spectrum.

The passive layer formed on painted specimens was examined by scanning electron microscopy after removal of the alkyd binder by means of a suitable solvent; then, the passive layer was scraped and its composition analyzed by FT-IR spectrometry.

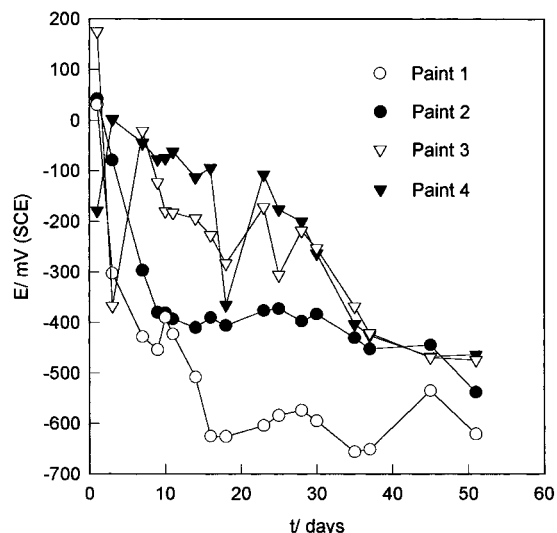
## Results and Discussion

**Accelerated Tests. (a) Salt Spray Test (ASTM B 117).** The rusting and blistering degrees after 720 h of the salt spray test are shown in Table 2. The anticorrosive protection achieved with paint 1, without topcoating, was poor. This behavior drastically changed when a complete painting scheme was applied; in this case, the steel surface, after coat removal, showed no signs of corrosion. The replacement of talc by calcium carbonate (paint 2) caused the corrosion degree to diminish, but failure at the scribe showed the greatest value of the series; blistering was also important. When talc was fully replaced by zinc oxide (paint 3), full protection and no blistering were observed. Similar results were obtained when talc was completely replaced by zinc oxide and calcium carbonate (50/50, paint 4); also in this case, failure at the scribe was reduced. The performance in the salt spray test was notably improved by the presence of zinc oxide and calcium carbonate in the pigment composition.<sup>10</sup>

**(b) Humidity Chamber Test.** Results obtained after 1600 h in the humidity cabinet test are presented in Table 3. Paints 3 and 4, containing zinc oxide in the pigment composition, showed no blistering. On the other hand, paints 1 and 2, pigmented with talc and calcium carbonate, showed the worst behavior. The anticorrosive performance was closely related with the observed blistering.

**Table 3. Rusting Degree (ASTM D 610) and Blistering (ASTM D 714) after 1600 h of Exposure in the Humidity Cabinet Test for Steel Panels Coated with the Anticorrosive Paints**

paint	blistering degree	rusting degree after paint removal
1	4D	4
2	6M	5
3	10	8
4	10	8

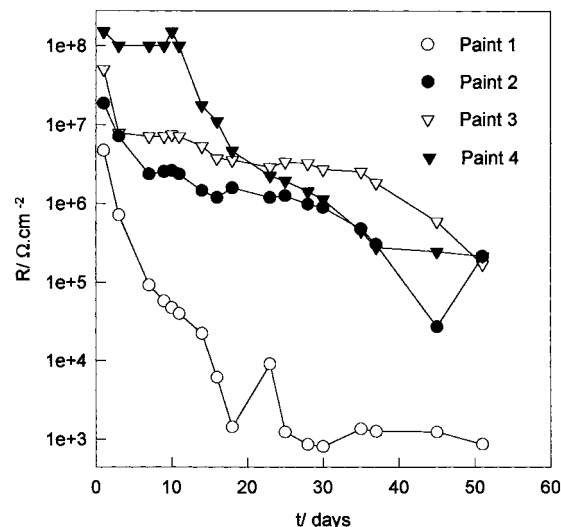


**Figure 1.** Corrosion potential of painted steel panels as a function of the exposure time in a 0.5 M sodium perchlorate solution.

**Electrochemical Measurements. (a) Corrosion Potential.** The corrosion potential was monitored for 51 days, this period being enough to detect the most important changes in the paint film (Figure 1). The corrosion potential of paint 1 derived quickly toward negative values, indicating that anticorrosive protection was lost. Paints 3 and 4 showed a very good performance, while paint 2 exhibited an intermediate behavior.

Taking into account that all pigment compositions contain the same proportion of calcium acid phosphate, the differences must be found in complementary pigments; the presence of calcium carbonate and zinc oxide in the pigment mixture was beneficial for steel passivation. The improvement of steel passivation was closely related to the pH value of the pigment suspension. The presence of these complementary pigments changed the pH value from 6.4 in paint 1 to 6.6 in paint 2, 7.0 in paint 3, and 7.1 in paint 4. Passivation of iron in phosphate solutions begins at pH values close to 7, at which phosphate and oxides could precipitate together.<sup>13</sup> It is important to point out that paints 3 and 4, for which talc was completely replaced, showed a noticeable ability to repassivate.

**(b) Ionic Resistance.** Among all tested paints, paints 4 ( $R > 10^8 \Omega \cdot \text{cm}^{-2}$ ) and 3 ( $R > 10^7 \Omega \cdot \text{cm}^{-2}$ ) showed the highest barrier properties. Paint 1 exhibited a lower barrier effect after 1 day of immersion which was lost quickly as time elapsed (Figure 2). It must be pointed out that the ionic resistance of paints 2–4 remained higher than  $10^6 \Omega \cdot \text{cm}^{-2}$  for 30 days. All tested paints had the same PVC/CPVC value and must have a similar porosity; however, at a given exposure time, they showed different ionic resistances. Paints containing calcium carbonate and zinc oxide developed the highest values. The most impervious film, at least during the initial phase of the immersion period, was



**Figure 2.** Ionic resistance of painted steel as a function of the exposure time in a 0.5 M sodium perchlorate solution.

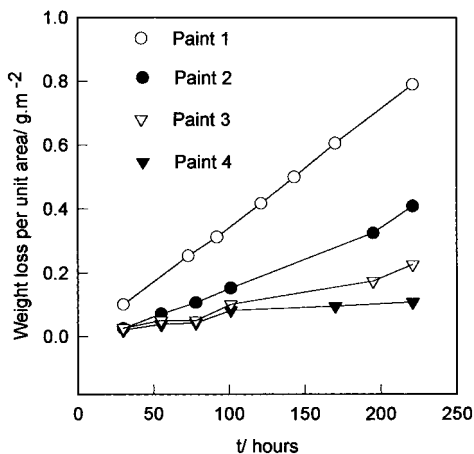
that obtained by replacing talc by calcium carbonate and zinc oxide (50/50). This was attributed to the reaction between zinc oxide and the alkyd resin to form zinc soaps. This interaction was confirmed by determining the zinc content in extracts obtained by milling together zinc phosphate and the alkyd resin employed in the research and zinc oxide with the alkyd binder for 24 h. The zinc content, expressed as milligrams of zinc cation per gram of resin, was found to be equal to 113 and 165, respectively.

The combined effect of a better steel passivation by a pH increase plus an enhanced barrier effect due to pigment–binder interaction caused paints 3 and 4 to perform in such an excellent way in the salt spray and the electrochemical tests. In the case of alkyds, the chemistry of drying followed by the stoichiometric neutralization of scission acids may be considered a goal to obtain barrier properties.

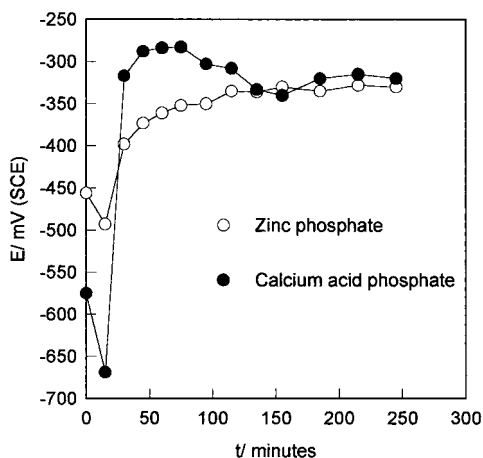
**(c) Polarization resistance,** as measured in this research, is not a true one because it includes the ionic resistance. However, in all cases it is higher (in some cases 10 times higher) than the ionic resistance, revealing the fact that the tested pigment has inhibitive properties.<sup>14</sup> Polarization resistance values above  $10^5 \Omega \cdot \text{cm}^{-2}$  were not measured because the system exhibited a linear response, indicating an ohmic control of the corrosion process due to the high barrier effect of tested paints. Polarization resistance for paint 1 was higher than the ionic one, indicating that the pigment inhibited steel corrosion. Polarization resistance for paints 3 and 4 showed that the corrosion process was controlled by the high barrier effect due to the presence of a very impervious film. Paint 2 exhibited an intermediate behavior.

The variation coefficient (standard deviation expressed as a percentage with respect to the arithmetic mean) in electrochemical tests was, as an average, 7%.

**Water Vapor Transmission.** The guideline to obtain efficient anticorrosive paints is not only to incorporate active anticorrosive pigments but also to decrease water and oxygen permeability as much as possible. Reduced water and oxygen permeability improves film adhesion, avoids adhesion loss by water, and diminishes, at the same time, undercutting and rusting at injured areas. As far as the PVC/CPVC ratio is concerned, all tested paints must have similar permeabilities; however, very



**Figure 3.** Water vapor transmission as a function of time (ASTM D 1653, test method B).

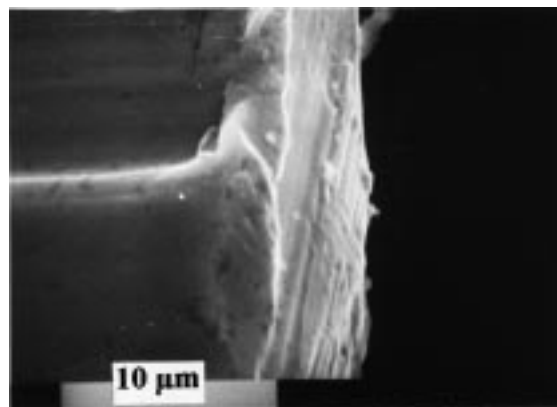


**Figure 4.** Corrosion potential of bare steel, as a function of the exposure time, in anticorrosive pigments suspended in a 0.01 M sodium perchlorate solution: zinc phosphate; calcium acid phosphate.

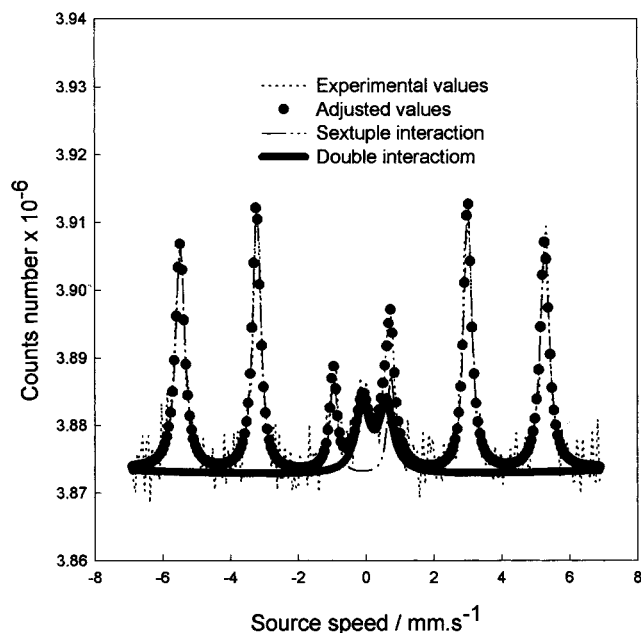
different behaviors were observed. Paint 4 showed the lowest permeability to water vapor and paint 1 the highest one (Figure 3). Concomitantly, paint 4 exhibited a very good performance in accelerated and electrochemical tests and paint 1 the poorest. As will be seen later, pigment–binder interaction may be responsible for the reduced permeability of this coating.

**Nature of the Passive Film.** The variation of steel corrosion potential as a function of time, in a calcium acid phosphate suspension (Figure 4), showed that it actually inhibited steel corrosion, shifting its potential toward more positive values than zinc phosphate did.

The steel plate kept immersed in the calcium acid phosphate suspension was examined by SEM, and the formation of an ordered layer on its surface was detected (Figure 5). The EDAX analysis showed that the main component of the passive layer was Fe; Ca and P were encountered in very low proportions (less than 1%). The Mössbauer spectrum of this layer revealed two types of interactions. One of them was a sextuple interaction corresponding to a magnetic material, in this case the base metal; the other was a doublet originated by the presence of a superparamagnetic phase with an isomer shift with respect to iron of  $0.309 \pm 0.2$  mm/s (Figure 6). This phase was identified as a  $\gamma$ -FeOOH<sup>15</sup> with a low crystallinity degree and a smaller particle size as was deduced from the broad line observed in the spectrum.



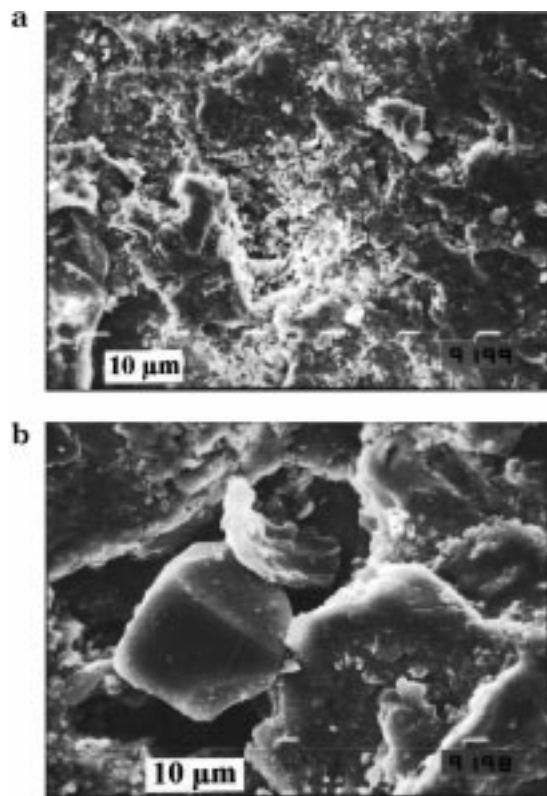
**Figure 5.** SEM micrograph of the passive layer formed on a steel substrate in a calcium acid phosphate suspension after 3 days of exposure.



**Figure 6.** Mössbauer spectrum of the passive layer formed on a steel substrate in a calcium acid phosphate suspension after 3 days of exposure.

When the steel plate was put in contact with the calcium acid phosphate suspension, some loose products appeared at the bottom of the container. To find the nature of the whole set of products formed in the reaction between steel and calcium acid phosphate, a moistened mixture of iron powder and calcium acid phosphate was allowed to react for 2 weeks and the resulting products were identified by FT-IR spectrometry. The analysis of the FT-IR spectra revealed that principally ferrous phosphate was formed (absorption bands at  $\sim 790$ ,  $872$ , and  $985$   $\text{cm}^{-1}$ ). Some ferric phosphate (absorption bands at  $\sim 670$  and  $1250$   $\text{cm}^{-1}$ ) together with unreacted calcium acid phosphate was also detected. It must be pointed out that all phosphates have a common strong absorption band at  $\sim 1050$ – $1100$   $\text{cm}^{-1}$ , so only distinctive bands were employed to identify different phosphates.

The passive layer formed under the paint film was also examined by SEM (Figure 7a,b). At a higher magnification ( $5000\times$ ), a rather compact film, constituted of crystals, was observed instead of the traditional globular morphology of deleterious ferric oxide. The FT-IR spectrum, obtained by scraping corrosion products



**Figure 7.** SEM micrograph of the passive layer formed on a steel substrate coated with an anticorrosive paint pigmented with calcium acid phosphate (paint 4) after 720 h of exposure in the salt spray cabinet: (a) magnification 2000 $\times$ ; (b) magnification 5000 $\times$ .

off the test panel, revealed the presence of ferric phosphate (absorption bands at  $\sim 550$ , 640, 670, and 1250  $\text{cm}^{-1}$ ), ferrous phosphate (absorption bands at  $\sim 872$  and 1450  $\text{cm}^{-1}$ ), and lepidocrocite with its characteristic frequency 1020  $\text{cm}^{-1}$ .<sup>16</sup>

From these experiences it was concluded that the passive film is mainly composed of ferric oxyhydroxide, which may be partially converted into ferric phosphate. Ferrous phosphate is an intermediate compound which is easily oxidized to ferric phosphate by atmospheric oxygen. Ferric phosphate was said to plug the pores of the ferric oxyhydroxide film.<sup>6</sup>

## Conclusions

(1) Calcium acid phosphate performance in anticorrosive paints was notably improved by incorporating suitable complementary pigments.

(2) The best results were achieved when calcium acid phosphate was employed with calcium carbonate and zinc oxide (50/50 by volume) as inert pigments.

(3) The improved anticorrosive performance was due to a combined effect: a higher barrier effect plus a more efficient passivation of steel substrate due to pH increase of the pore solution.

(4) The passive film seemed to be composed of an ordered layer of ferric oxyhydroxide and small amounts of ferric phosphate.

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