

STEEL CORROSION PROTECTION BY MEANS OF ALKYD PAINTS PIGMENTED WITH CALCIUM ACID PHOSPHATE

PINTURAS ALQUIDICAS A BASE DE FOSFATO ACIDO DE CALCIO PARA LA PROTECCION ANTICORROSIVA DEL ACERO

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SUMMARY

The use of classic anticorrosive pigments is being more and more restricted by increasing environmental concerns; they are gradually 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 inhibitive pigment introducing a careful selection of complementary pigments in order to achieve an efficient anticorrosive protection. Several paints were prepared and tested through accelerated and electrochemical tests. The nature of the passive film was also studied.

Paints containing zinc oxide and calcium carbonate (50/50) showed the best performance and a higher resistance in the salt spray test. Zinc oxide and calcium carbonate decreased film permeability and improved steel passivation.

The passive film was composed by a ferric oxyhydroxide film whose pores became plugged by ferric phosphate.

Keywords: *calcium acid phosphate, alkyd anticorrosive paints, zinc oxide, calcium carbonate.*

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 cancerigenous risk.

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The long awaited reduction in usage of classical active pigments has induced considerable search for adequate alternative products for more than 15 years. Particular attention has been paid to zinc phosphate since it was found that its effectiveness could be improved by controlled chemical modification of its structure with suitable elements or by changing the anion orthophosphate by polyphosphate one [1-8].

Comparative anticorrosive performance of calcium acid phosphate and zinc phosphate was established in a previous paper [9, 10].

The aim of this paper is to study the anticorrosive properties of calcium acid phosphate as inhibitive pigment, introducing an important modification with respect to authors' previous studies [9, 10]. 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.

EXPERIMENTAL

Paints composition and manufacture

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 a medium alkyd resin. It showed the characteristic peak of alkyds at 1275 cm^{-1} and other peaks assigned to the stretching of the C-H bond in oil (2870 and 2930 cm^{-1}), the stretching of the C=C bond (1490 , 1580 and 1600 cm^{-1}) and to the bending of the benzene ring (705 and 745 cm^{-1}) [11].

Pigment. Calcium acid phosphate was employed as anticorrosive pigment and its content was 30% by volume with respect to the total pigment formula. Other pigments such as titanium dioxide, magnesium silicate, calcium carbonate, zinc oxide and barium sulphate were used as complementary pigments. The PVC/CPVC relationship for all the paints was 0.8, resulting this value in a similar free binder content in all cases. Paints solids percentages, expressed as % by volume, are shown in Table I.

Paints preparation. It was carried out employing a ball mill with 3.3 liters jar. The resin solution was added firstly and pigments were incorporated later. The system was dispersed during 24 hours to achieve an acceptable dispersion degree [12].

Paints application. They were applied by means of a spray gun on ASTM 1010 steel panels ($15.0 \times 7.5 \times 0.2\text{ cm}$) up to a thickness of $75 \pm 5\text{ }\mu\text{m}$. Tested panels were previously sandblasted to Sa 2 ½ (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 and the other with a complete system (a conventional alkyd enamel was used as a topcoat) up to a film thickness of $125 \pm 5 \mu\text{m}$.

Table I

Solids in paint composition (% 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 sulphate	9.6	9.6	9.6	9.6
Alkyd resin	46.0	46.0	46.0	46.0

Laboratory tests

Standardized 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 performance of these paints.

Water vapour transmission was evaluated to determine coating permeability.

Finally, the nature of the passive layer was investigated by scanning electron microscopy (SEM) on both, bare steel submerged in a pigment suspension and at the metal/coating interface.

Accelerated tests

Salt spray test (ASTM B 117). A scratch line was made through the coating with a sharp instrument so as to expose the underlying metal to the aggressive environment. The panels were periodically observed, without removing the coating, to assess both the rusting degree (ASTM D 610) and the failure at the scribe (ASTM D 1654). In all cases experiences were carried out in triplicate, determining the mean value of the obtained results. Results after 720 hours exposure are displayed in Table II.

Humidity chamber test. Another series of panels coated with the anticorrosive paints alone, was placed in the humidity chamber at $38 \pm 1^\circ\text{C}$ for 1600 hours (ASTM D 2247). The blistering degree was established according to the ASTM D 714 standard specification.

Table II

Rusting degree (ASTM D 610), failure at the scribe (ASTM D 1654) and blistering (ASTM D 714) after 720 hours exposure in the salt fog chamber for steel panels covered with the selected painting systems

Painting system	Anticorrosive paint			Anticorrosive paint + topcoat		
	Rusting degree			Blistering	Rusting degree	
Paint	Without removing the coat	After coat removal	Failure at the scribe	Without removing the coat	Without removing the coat	After coat removal
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

Electrochemical measurements

Corrosion potential. The electrochemical cells to measure corrosion potential of painted steel as a function of time were constructed by delimiting 3 cm² circular zones on the painted surface. An acrylic tube, with one flat end and 7 cm high, was placed on the specimen and filled with the electrolyte (0.5 M sodium perchlorate solution). Corrosion potential of coated steel was measured against a saturated calomel electrode (SCE) with a high impedance voltmeter.

Ionic resistance. The resistance between the painted steel substrate and a platinum electrode was also measured 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.

Polarization resistance. The polarization resistance of painted panels was determined as a function of the immersion time for specimens whose ionic resistance was less than 10⁵ Ω.cm⁻². The electrochemical cell had three electrodes, a calomel one as reference and the counterelectrode was a platinum grid. The voltage swept was ±10 mV, starting from the corrosion potential. Measurements were done employing an EG&G PAR Potentiostat/Galvanostat, Model 273A and the software SOFTCORR 352. Polarization resistance of uncoated steel was also monitored as a function of the immersion time.

Water vapour transmission

Water vapour transmission was evaluated according to ASTM D 1653, test method B, applying the paint films by means of a brush on a filter paper (dry film thickness 70 μm). Perm cups consisting of a container made of non-corroding, impervious to water and water vapour material, 25 cm^2 area, were employed (Fig. 1).

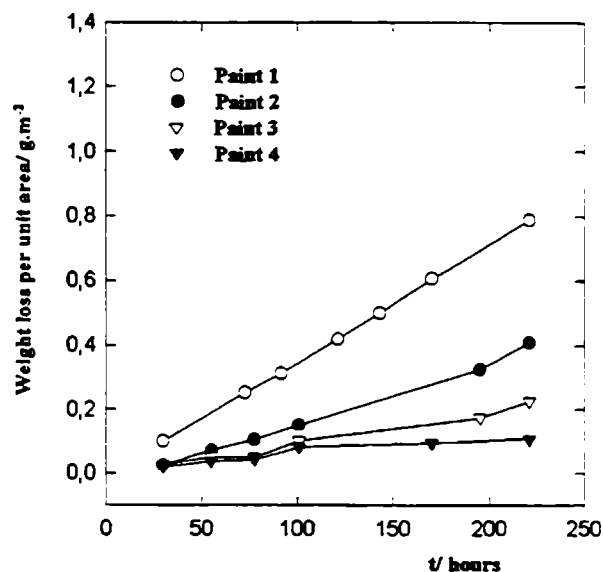


Fig. 1. Water vapour transmission as a function exposure of time (ASTM D 1653, test method B).

The nature of the passive film

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 nature of the passive film formed on the steel surface was studied by scanning electron microscopy (SEM) 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 IR spectrum.

The passive layer formed on painted specimens was examined by SEM after removing the alkyd binder by means of a suitable solvent; then, the passive layer was scraped and its composition analysed by IR spectrometry.

RESULTS AND DISCUSSION

Accelerated tests

Salt spray test (ASTM B 117). The rusting and blistering degree after 720 hours are shown in Table II. The anticorrosive protection achieved with paint 1, without topcoating, was poor and closely related with the blistering observed in this case which was the greatest of the

series (4D grade). This behaviour drastically changed when a complete painting system was applied since after coat removal no signs of corrosion were found.

The results obtained show that replacing talc with calcium carbonate (paint 2) the corrosion degree diminished but failure at the scribe showed the greatest value of the series; blistering was also important. When the replacement was made with zinc oxide (paint 3) a full protection and no blistering were observed. Similar results were obtained when talc was completely replaced by zinc oxide and calcium carbonate (paint 4); but in this case the protection at the scribe was improved. The performance in the salt spray test was notably improved by the presence of zinc oxide and calcium carbonate in the pigment composition [10].

Humidity chamber test. Results obtained after 1600 hours in the humidity cabinet test are presented in Table III. 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 behaviour. The anticorrosive performance was in accordance with the observed blistering.

Table III

Rusting degree (ASTM D 610) and blistering (ASTM D 714) after 1600 hours exposure in the humidity cabinet test for steel panels covered with the anticorrosive paint alone

Paint	Blistering	Rusting degree after coat removal
1	4D	4
2	6M	5
3	10	8
4	10	8

Electrochemical measurements

Corrosion potential. Corrosion potential was monitored for 51 days, being this period enough to detect the most important changes in paint film (Fig. 2). Paints 3 and 4 showed the best behaviour in this test while paints 1 and 2 the worst. Taking into account that all pigment compositions contained the same volume of calcium acid phosphate, the differences must be attributed to in the complementary pigments used in this research. The presence of calcium carbonate and zinc oxide in the pigment mixture improved steel passivation, which was closely related to the pH value of the pigments suspension. The presence of these complementary pigments changed the pH value from 6.4 in paint 1 to 6.6 in paint 2, 7 in paint 3 and 7,1 in paint 4. Passivation of iron in phosphate solution begins at pH values close to 7 because at this pH phosphate and oxides could precipitate together [13]. It is important to point out that paints 3 and 4, in which talc was not used, showed a noticeable ability to repassivate. It is

thought that this improved steel passivation is responsible for the better anticorrosive performance observed in the salt spray test.

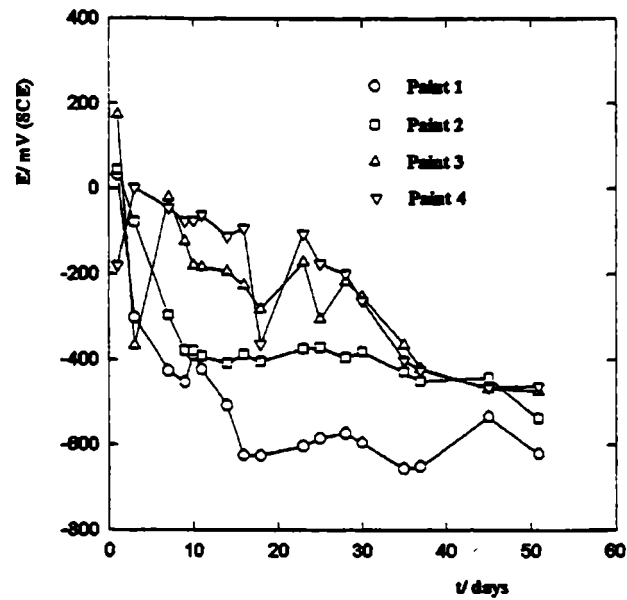


Fig. 2.- Corrosion potential of painted steel panels as a function of the exposure time, in 0.5 M sodium perchlorate solution.

Ionic resistance. Among all tested paints, paint 4 ($R > 10^8 \Omega \cdot \text{cm}^2$) and paint 3 ($R > 10^7 \Omega \cdot \text{cm}^2$) showed the highest barrier properties (Fig. 3) which was maintained greater than $10^6 \Omega \cdot \text{cm}^2$ for 30 days. All the paints had the same PVC/CPVC value and the coat must have the same porosity [14]; however, paints containing calcium carbonate and zinc oxide showed the highest ionic resistance value. The most impervious film, at least during the initial phase of the immersion period, was that obtained replacing talc by calcium carbonate and zinc oxide (50/50).

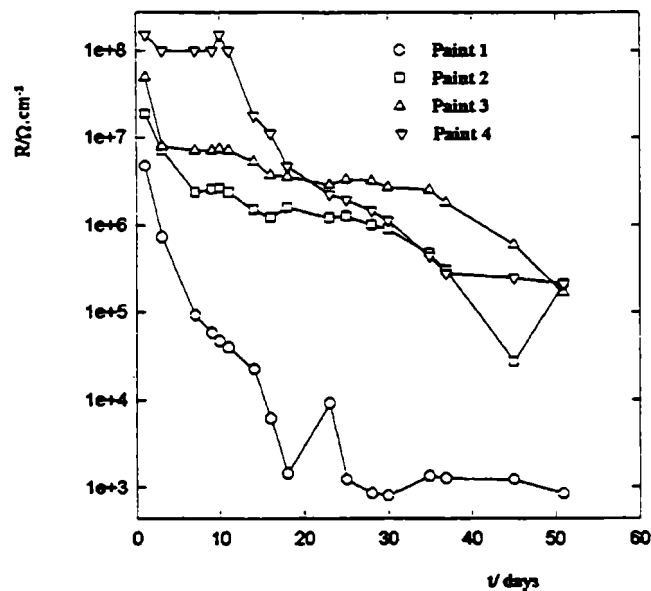


Fig. 3- Resistance of painted steel as a function of the exposure time in 0.5 M sodium perchlorate solution.

The reduced ionic permeability was due to the reaction between zinc pigments and the alkyd resin. This interaction was confirmed by determining the zinc content in extracts obtained by milling together either zinc phosphate and the alkyd resin or zinc oxide with the alkyd binder for 24 hours. The extracts were dried at 110 °C, calcined to eliminate organic matter and diluted with hydrochloric acid (1+1). The zinc content was determined by atomic absorption and was found to be equal to 113 and 165 mg of zinc cation per gram of resin, respectively.

Considering Funke's opinion about the fact that the future of corrosion control by organic coatings more likely lies in developing the barrier properties of the coat [15], the findings of this research are relevant.

Polarization resistance. As a general rule, it must be said that polarization resistance 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; it stood higher than 0,5 MΩ.cm⁻² during the test period and it was impossible to measure it accurately because of instrumental limitations.

Water vapour transmission

To obtain efficient anticorrosive paints it is necessary not only the addition of active anticorrosive pigments but also the reduction of water and oxygen permeability as much as possible. The reduction of water uptake avoids adhesion loss at the metal-coating interface diminishing, at the same time, undercutting and underfilm rusting of injured coatings. As far as the PVC/CPVC ratio is concerned all tested paints must have similar permeabilities [14]; however, paint 4 showed the lowest permeability to water vapour and paint 1 the highest one (Table IV). At the same time, paint 4 exhibited a very good performance in accelerated and electrochemical tests and paint 1 the poorest. This behaviour may be partially related to the capacity of coatings to restrain the passage of water vapour as time elapsed (Fig. 1); paint 4 showed the lowest weight loss as a function of time and paint 1 the highest, as it could be deduced from the slopes of the both curves.

Table IV

Water vapour transmission after 24 hours (g m⁻²)

Paints	1	2	3	4
Water vapor transmission	0.10830	0.02259	0.04090	0.01066

The nature of the passive film

The variation of steel corrosion potential, as a function of time, in the presence of a calcium acid phosphate suspension (Fig. 4), showed that it inhibited steel corrosion and that caused potential shiftings towards more positive values with respect to zinc phosphate.

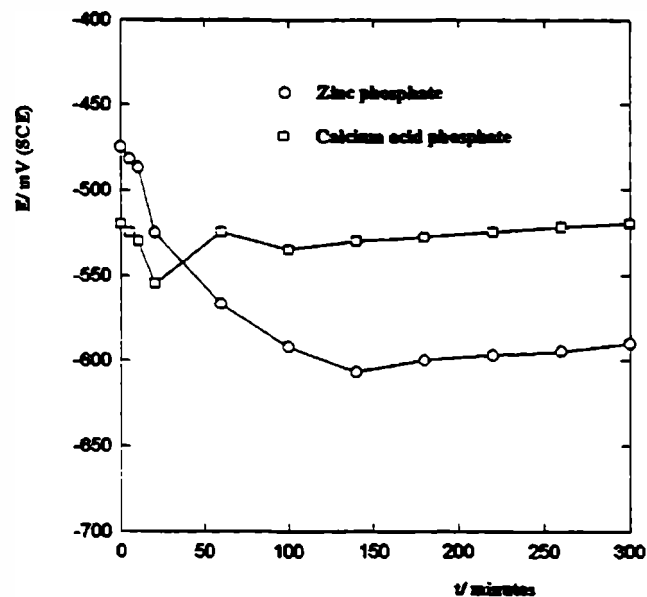


Fig. 4.- Corrosion potential of bare steel, as a function of the exposure time, in anticorrosive pigment suspensions in 0.5 M sodium perchlorate solution: a) zinc phosphate, b) calcium acid phosphate.

The steel plate kept in contact with the calcium acid phosphate suspension was examined by SEM and it was detected the formation of an ordered layer on the metallic surface (Fig.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%). This layer was identified by Mössbauer spectroscopy and the analysis of the spectrum 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 corresponding to a superparamagnetic phase with an isomer shift with respect to iron of 0.309 ± 0.2 mm/s (Fig.6). This phase was identified as an FeOOH [16] with a low crystallinity degree and a smaller particle size as it was deduced from the broad line observed in the spectrum.

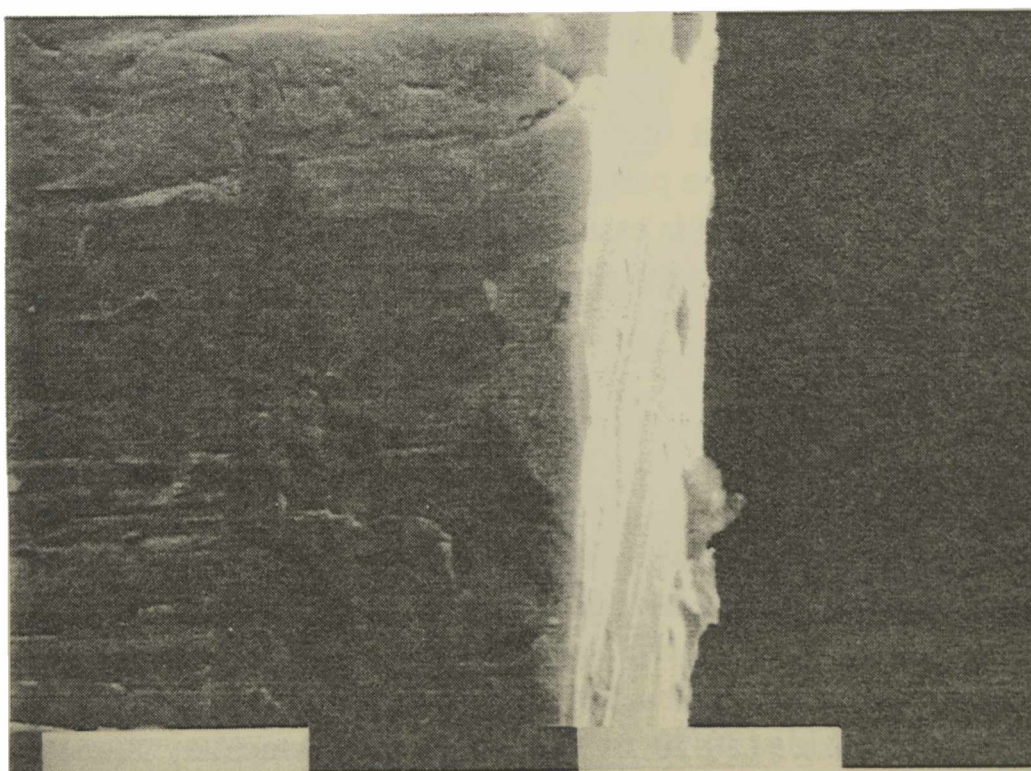


Fig. 5.- SEM photomicrograph of the passive layer formed on a steel substrate in a calcium acid phosphate suspension after 3 days exposure.

When the steel plate was put in contact with the calcium acid phosphate suspension, some loose products appeared at the bottom of the container. In order to know 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 during 2 weeks and the resulting products identified by IR spectrometry. The spectra revealed that ferric phosphate was formed (absorption bands at ~ 1050 , 1100 and 1270 cm^{-1}).

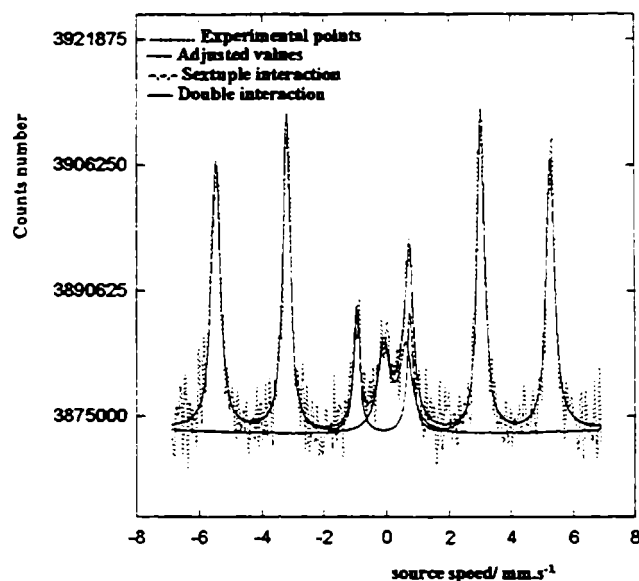


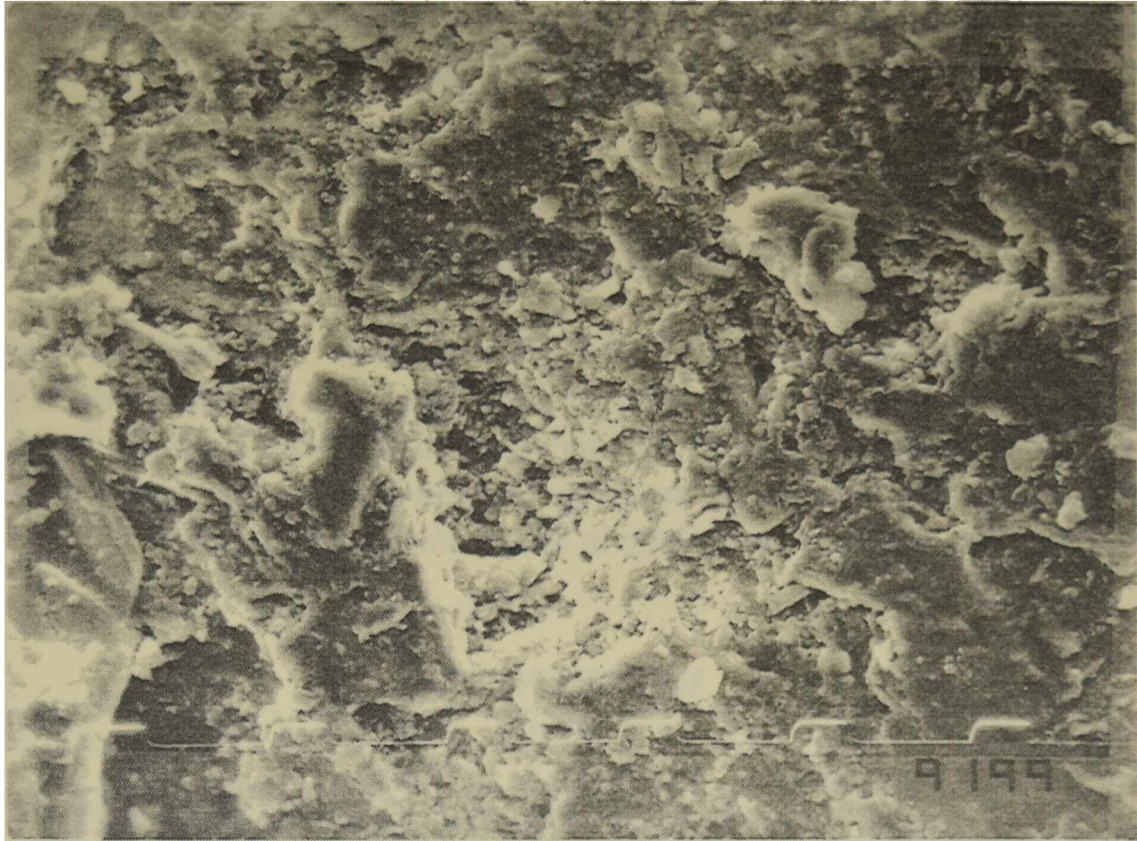
Fig. 6.- Mössbauer spectrum of the passive layer formed on a steel substrate in a calcium acid phosphate suspension after 3 days exposure.

The passive layer formed under the paint film was also examined by SEM (Figs 7a and 7b). Instead of the globular morphology of deleterious ferric oxide, a rather compact film was observed. It showed, at higher magnifications (5000X), the presence of crystals. The IR spectrum, obtained by scrapping corrosion products off the test panel, revealed the presence of ferric phosphate (absorption bands at ~ 1100 and 1270 cm^{-1}) and ferrous phosphate (absorption bands at ~ 743 , 876 , 1070 and 1270 cm^{-1}).

From these experiences it was concluded that the passive film is mainly composed of ferric oxyhydroxide which may be partially converted in 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 [6].

CONCLUSIONS

- 1) Calcium acid phosphate performance in anticorrosive paints was highly 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 complementary pigments.



(a)



(b)

Fig. 7.- SEM photomicrograph of the passive layer formed on a steel substrate coated with an anticorrosive paint pigmented with calcium acid phosphate (Paint 4) after 720 exposure in the salt spray cabinet; a) 2000X, b) 5000X.

- 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 solution retained in the coating pores.
- 4) The passive film was to be composed of an ordered layer of ferric oxyhydroxide and small amounts of ferric phosphate.

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