

Role of calcium acid phosphate as corrosion inhibitive pigment

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Chromate based anticorrosive pigments are gradually being replaced because of their toxicity and carcinogenic properties. Zinc phosphate has been used to replace chromates but has led to contradictory results, its main difficulty being low solubility. Calcium acid phosphate, which has a higher solubility, could replace zinc phosphate. Evaluations of the degree of rusting on painted panels, corrosion rate measurements, and electrochemical studies (corrosion potential measurements and polarisation curves) have shown that calcium acid phosphate is better than zinc phosphate and is comparable to zinc tetroxychromate as an anticorrosive pigment in a phenolic chlorinated rubber binder. An advantage from an ecological point of view is that calcium ions provide less contamination than zinc ions.

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INTRODUCTION

The toxicity and carcinogenic properties of chromate based anticorrosive pigments is causing concern and it has been suggested by Kukla *et al.*¹ that zinc chromate could be partially replaced by other anticorrosive pigments such as zinc phosphate and phosphonic acid derivatives to obtain primers with reduced toxicity.

Zinc phosphate is being increasingly used as an alternative pigment,² but contradictory experimental results have been obtained. Excellent anticorrosive performance for zinc phosphate pigmented primers using a linseed oil binder has been reported³ and other binders such as phenolic-tung, nitrocellulose, chlorinated rubber, vinyl polymers, and epoxies have been used.²⁻⁸ The success of zinc phosphate in alkyd resin paints exposed to industrial atmospheres and its poor behaviour in rural areas have been reported^{4,9} and the same has occurred with epoxy binders.

The anticorrosive behaviour of zinc phosphate depends on the binder⁵ and could be improved by the employment of suitable additives.^{5,10} Other inorganic phosphates have been proposed⁷ and modified zinc phosphate based pigments have been introduced.¹⁰ One disadvantage of zinc phosphate is its relatively high cost of production.

Zinc phosphate in paint is more resistant than chromate to sulphate and chloride ions and it improves the top coat adhesion.⁵ However, the paint is more susceptible to attack and blistering by fungi.¹¹ Electrochemical tests showed that zinc chromate was more effective than zinc phosphate.¹²

It has been suggested that calcium acid phosphate could be employed instead of zinc phosphate giving similar anticorrosive properties and reduced costs. (Calcium salts are cheaper than zinc salts.) Solubility product constant values for zinc phosphate ($Zn_3(PO_4)_2$) and calcium acid phosphate ($CaHPO_4$) are 9.1×10^{-33} and 5.6×10^{-7} respectively,¹³ indicating that the replacement is possible and advantageous since calcium acid phosphate is 5000 times more soluble than zinc phosphate.

In recent literature calcium acid phosphate has not been used as a sole inhibitive pigment in anticorrosive paints. However, a core anticorrosive pigment based on zinc phosphate and manganese phosphate with calcium acid phosphate has been prepared.¹⁴ Reichert *et al.*¹⁵ used calcium acid phosphate neutralised with zinc, calcium oxides, and calcium carbonate in a solvent free formulation. Chromy and Kaminska⁷ reported the use of barium acid phosphate but it must be taken into account that barium salts are toxic.

The aim of this paper is to study the anticorrosive properties of calcium acid phosphate in a phenolic

chlorinated rubber binder. The results are compared with those using zinc phosphate and zinc tetroxychromate. In all cases, 12% pigment volume concentration (pvc) of anticorrosive pigment was used and the final pigment loading was 34%. Three stages were planned.

The first stage involved obtaining information about the pigments' anticorrosive behaviour in practice. Paints employing calcium acid phosphate, zinc phosphate, and zinc tetroxychromate in a phenolic chlorinated rubber binder were prepared and all three were submitted to a salt spray test.

The extent to which the corrosion rate of steel could be reduced by the pigment was evaluated by measuring the corrosion rate of steel in pigment suspensions and comparing the results with a blank. This information allowed comparison of the actual efficiency of the pigment with the zinc phosphate and the zinc tetroxychromate.

The third stage involved a series of electrochemical tests to establish their anticorrosive properties. Test were carried out according to the current procedures described in the literature, employing a suspension of the appropriate pigment.¹⁶⁻¹⁸

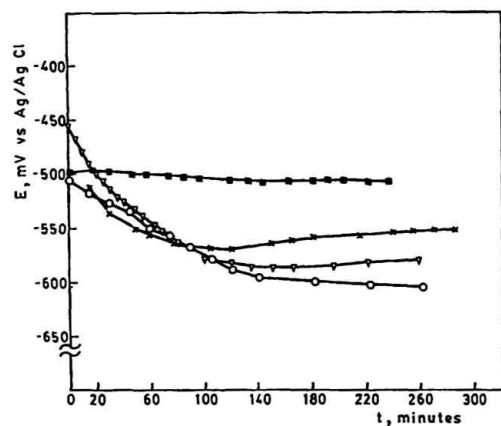
The way in which the corrosion potential varied as a function of time in sulphate containing media was studied, as well as the voltammetric characteristics of iron in the same media. The corrosion potential values indicated whether the substrate was protected by the pigment but gave no information about the nature of the substrate passivity. This information was obtained from polarisation curves of the system under test. The composition of the protective layer was determined analytically.

EXPERIMENTAL

The anticorrosive properties of calcium acid phosphate were compared with those of zinc phosphate and zinc tetroxychromate. Experiments were conducted at least in triplicate and, where possible, the variation coefficient was calculated and specified in the text.

Paint application

Three anticorrosive paints were prepared employing calcium acid phosphate, zinc phosphate, and zinc tetroxychromate. Tetroxychromate based formulations have shown good performance with chlorinated rubber phenolic varnish as binder.¹⁹ Except for the anticorrosive pigment the paints had a similar composition and the same pvc value (Table 1). The particle size dispersion corresponded to 5 on the Hegman scale. Paints were applied on sandblasted AISI 1010 steel panels by brushing ($80 \pm 5 \mu\text{m}$ film thickness).



○ blank, 0.5M Na₂SO₄; ▽ zinc phosphate; × calcium acid phosphate; ■ zinc tetroxychromate

1 Iron electrode potential as function of time for suspensions of anticorrosive pigments in 0.5M Na₂SO₄

Salt spray test

The panels were subjected to the ASTM B117 salt spray test for 1000 h, after which the film was removed by means of an appropriate solvent blend. The steel panel was visually examined and classified according to ASTM D610 to determine the degree of corrosion.

Corrosion rate of steel in pigment suspensions

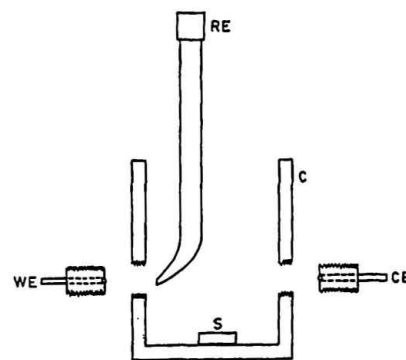
The relative corrosion rate of steel in the presence of the different pigments was determined by rotating 25 × 55 mm steel plates in the pigment suspensions for 24 h. At the end of the test the corrosion products were removed electrolytically in 30% HCl using a graphite anode at a current density of 0.6 mA cm⁻². In each case the amount of dissolved iron was determined by conventional analytical techniques¹³ and atomic absorption. Blank tests were conducted in 0.1M Na₂SO₄ without any pigment present and the results are given in Table 2. The variation coefficient for the determination of the corrosion rate was found to have an average value of 4.7%.

Corrosion potential measurements

The corrosion potential variation of iron as a function of the immersion time in 0.5M Na₂SO₄ (blank) and in suspensions of anticorrosive pigment (calcium acid phosphate, zinc phosphate, and zinc tetroxychromate) in the same electrolytic solution was measured. In each case the suspensions were allowed to stand for at least 24 h before taking the measurements. A 15 mm diameter spectroscopical pure iron electrode and a silver/silver chloride electrode were used. The calcium acid phosphate slurry pH value was also measured. Measurements were carried out using a 701 A model Orion voltmeter and the results are plotted in Fig. 1. The variation coefficient for the corrosion potential measurement, at a given exposure time, was 1.7%.

Table 1 Composition of tested paints, vol.-%

Calcium acid phosphate	0	0	6.00
Zinc tetroxychromate	0	6.00	0
Zinc phosphate	6.00	0	0
Iron oxide (Fe ₂ O ₃)	5.17	5.47	5.21
Barium sulphate	5.08	5.76	5.06
Phenolic varnish	14.4	15.7	14.6
Chlorinated rubber	9.90	10.8	10.1
Tricresyl phosphate	5.32	5.59	5.15
Aluminum stearate	1.53	1.48	1.48
Solvent blend	52.6	49.2	52.4
Pigment vol. conc.	34.0	34.0	34.0



2 Electrolytic cell: WE = iron working electrode; RE = Ag/AgCl reference electrode; CE = platinum counter electrode; S = magnetic stirrer; C = acrylic beaker

Polarisation curves

Polarisation curves for spectroscopically pure iron in both 0.5M Na₂SO₄ and suspensions of calcium acid phosphate, zinc phosphate, and zinc tetroxychromate in 0.5M Na₂SO₄ were obtained using a Ag/AgCl reference electrode and a 5 mm diameter platinum disc as counter electrode. The electrolytic cell is shown in Fig. 2. The polarisation curves were obtained using a Beckman Electroscan 30 at 4 mV s⁻¹ scan rate, starting the scanning in the vicinity of the corrosion potential. The electrochemical properties of the iron electrode were not significantly different from those of the AISI 1010 steel.

Composition of protective film

In order to determine the composition of the protective film, 2 × 3 cm steel plates were exposed to a stirred calcium acid phosphate suspension with and without polarisation at the peak potentials observed in the anodic voltammograms (Fig. 3). Corrosion products were analysed to determine calcium and iron by atomic absorption (taking into account the possible influence of the phosphate anion) and phosphate by a colorimetric procedure.²⁰ The results are given in Table 3.

The iron electrodes and the steel plates were mechanically polished with 120 emery paper and then degreased with alkaline substances such as calcium hydroxide before starting each experiment. In all cases the solutions and the suspensions were stirred to avoid pigment settlement. The calcium acid phosphate was prepared in the laboratory according to current procedures described in the literature.²¹

RESULTS AND DISCUSSION

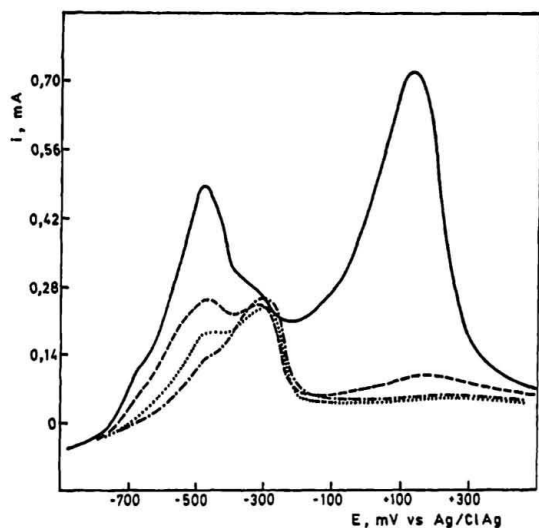
Calcium acid phosphate protective action

The degree of rusting of painted steel surfaces in the 1000 h salt spray test was evaluated according to ASTM D610.

Table 2 Determination of corrosion rate of steel in presence of different anticorrosive pigments

Pigment	Corrosion rate in terms of dissolved iron, mg m ⁻² /day	Corrosion reduction factor*
Blank, 0.1M Na ₂ SO ₄	14 600	1.00
Zinc tetroxychromate	2600	5.61
Zinc phosphate	4000	3.65
Calcium acid phosphate	3300	4.42

*The corrosion reduction factor is the relationship between the iron corrosion rate for the blank and the iron corrosion rate in the presence of an anticorrosive pigment.



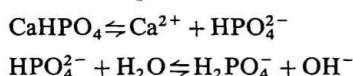
— sweep 1; ---- sweep 2; sweep 3; - - - - sweep 6
 3 Anodic polarisation curve for iron electrode in presence of calcium acid phosphate suspension: scan rate 4 mV s^{-1}

The panels coated with the calcium acid phosphate pigmented paint were graded 8 and the undercutting rusting was equal to or less than 3 mm. The panels coated with the zinc phosphate pigmented paint were graded 4–5 and a similar undercutting rusting to that of calcium acid phosphate was detected. It was observed that areas with small pits were grouped on the surface and the pit diameters were generally less than 0.5 mm. The panels coated with the tetroxychromate pigmented paint were graded 7 and the undercutting rusting reached 6 mm. Localised large oxide spots were observed on the steel surface.

The results in Table 2 show that the calcium acid phosphate reduced the corrosion rate of steel by a factor of 4.4. This is of the same order as the factor by which the oxygen limiting current was decreased. It was also observed that the calcium acid phosphate exhibited better corrosion protection than the zinc phosphate. Zinc tetroxychromate decreased the steel corrosion rate by a factor of 5.61, but after 24 h exposure the steel plate showed signs of localised corrosion.

Corrosion potential as function of time

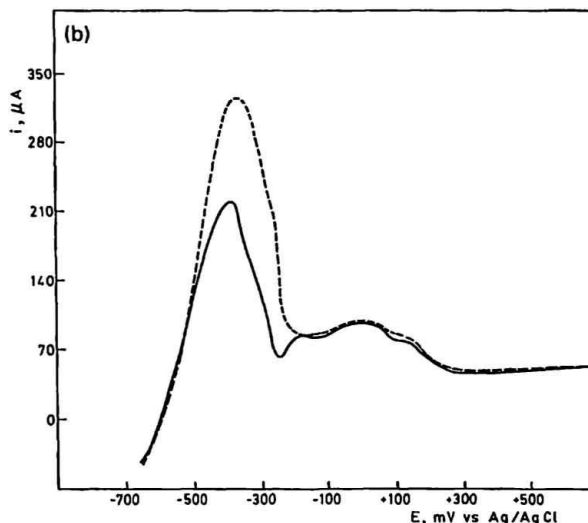
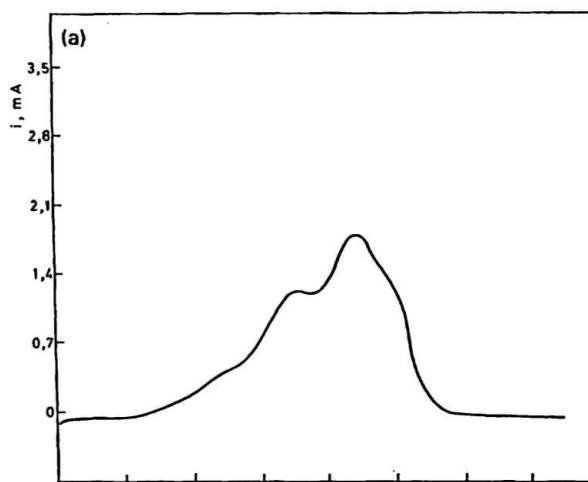
When calcium acid phosphate dissolves the following reactions take place



The slurry pH value was found to be close to 7. This showed that the steel surface is in contact with an equimolar solution of HPO_4^{2-} and H_2PO_4^- (Ref. 13) and, of course, calcium ions.

Table 3 Composition of anodic film formed on steel substrate in presence of calcium acid phosphate solution with and without applied polarisation, mg m^{-2}

Applied potential, mV(Ag/AgCl)	Exposure time	Composition, mg m^{-2}		
		Iron	Calcium	Phosphate
0	24 h	67200	2700	2710
-475	1000 s	19000	3200	2900
-300	1000 s	15300	2130	2030
+130	1000 s	18700	2130	2900



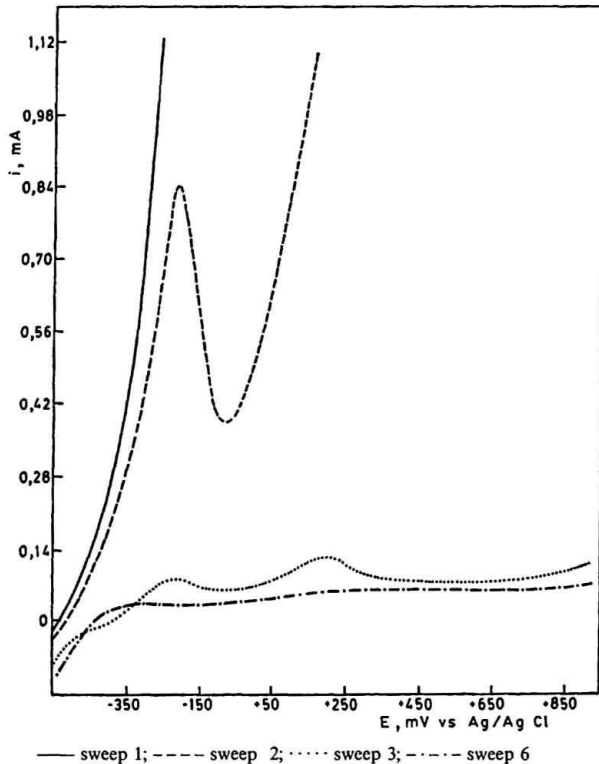
a sweep 1; b — sweep 2; ---- sweep 6
 4 Anodic polarisation curve for iron electrode in $0.5\text{M Na}_2\text{SO}_4$: scan rate 4 mV s^{-1}

From data plotted in Fig. 1 it may be seen that the calcium acid phosphate suspension produced a corrosion potential shift towards more positive values with respect to both the blank sodium sulphate solution and the zinc phosphate suspension. Calcium acid phosphate stabilised the iron surface, forming a bluish film. When zinc tetroxychromate was employed oxide spots appeared on the electrode surface.

Anodic polarisation curves

The anodic polarisation curve for the iron electrode in a calcium acid phosphate suspension (Fig. 3) showed a peak in the potential range $-480 \pm 10 \text{ mV}$ with a shoulder (-300 mV) and a second peak. The first peak may correspond to the spontaneous corrosion process associated with the growth and adhesion to the substrate of a first layer composed mainly of ferrous compounds. The evidence for this explanation is that the peak did not appear in the voltammogram during the first sweep when the electrode was kept in contact with the suspension for a period of time before polarising the electrode. (Such behaviour was not observed with the blank sodium sulphate solution.) In successive sweeps the peak current decreased continuously and the peak appeared at more positive values.

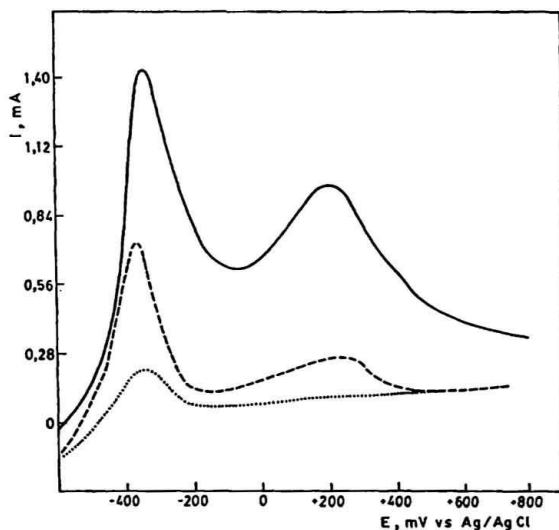
The iron electrode in $0.5\text{M Na}_2\text{SO}_4$ had a similar voltammogram after the first sweep with two major peaks (Fig. 4). The first peak in the $-400 \pm 20 \text{ mV}$ range showed



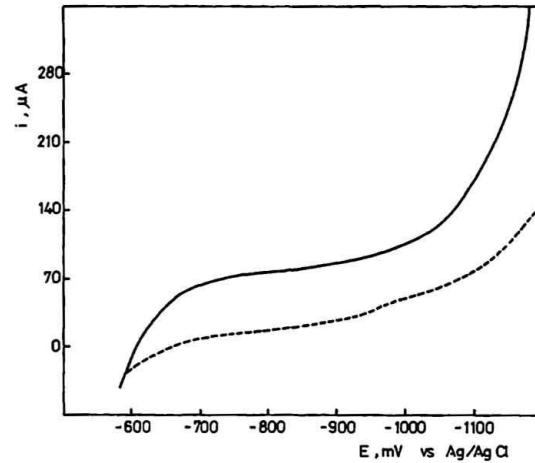
5 Anodic polarisation curve for iron electrode in presence of zinc phosphate suspension

a peak current which increased continuously in the successive sweeps. (The opposite behaviour was observed in the presence of calcium acid phosphate, where the current variation decreased continuously with each potential sweep.) This first peak is thought to describe what happens during the spontaneous corrosion process. The smaller peak area obtained in the presence of calcium acid phosphate was attributed to the formation of a less porous film.²²

These experiments led to the conclusion that the film which originated on the electrode in the calcium acid phosphate pigmented paint gave the iron surface certain protective and stabilising properties. The drift of the corrosion potential towards more positive values with time confirms this statement. Each voltammogram (Figs. 3–6)



6 Anodic polarisation curve for iron electrode in presence of zinc tetroxychromate suspension



7 Cathodic polarisation curve for iron electrode in presence of calcium phosphate suspension

exhibited a second peak which could correspond to the oxidation of ferrous to ferric compounds.

However, no passivation occurred because high currents were observed due to the iron substrate oxidation through pores of the film. This would indicate that the pigment is suitable for use in paints since in this case the low film permeability limits the water and oxygen uptake.

The anodic polarisation curves for the iron electrode in a zinc phosphate and in a zinc tetroxychromate suspension (Figs. 5 and 6) showed voltammograms with two peaks and higher currents.

Cathodic polarisation curves

The analysis of the cathodic polarisation curves for an iron electrode in the calcium acid phosphate suspension showed that protective corrosion products might also form as a consequence of the cathodic reaction. The evidence for this is that the oxygen reduction current decreased by a factor of about 5 (Fig. 7). Sometimes the complete inhibition of the oxygen reduction reaction was seen and a shift in the decomposition overpotential of about -200 mV occurred. When zinc tetroxychromate was used as an anticorrosive pigment a similar effect in the oxygen reduction wave was observed. The anodic film formed in sulphate solutions did not affect the oxygen current. These results are similar to those of Szklarska-Smialowska and Mankowski,²³ who studied the oxygen reduction of iron in solutions containing small amounts of calcium and phosphate ions. They did not study the formation and properties of the anodic film.

The analysis of the polarisation curves showed that calcium acid phosphate acted both as a cathodic and an anodic inhibitor.

Composition of protective film

The protective film formed on the steel substrate in the presence of calcium acid phosphate is mainly composed of iron oxides with calcium and phosphate ions present to a lesser extent (Table 3) and the results agree with those previously reported.³ The molar ratio of $\text{Ca}^{2+}/\text{PO}_4^{3-}$ is almost constant in most cases and has a value close to 2.5 (Table 3). This fact and the presence of a bluish film on the surface led to the conclusion that a protective compound formed on the plate. However, its composition must be further investigated. The relatively high amounts of iron detected in the analysis are in accordance with the polarisation data. They indicate that the base metal could not be protected by this film in the presence of large

amounts of water and oxygen; but this is not the case with a coated metal which restricts the amount of oxygen and water.

When zinc phosphate is employed as an anticorrosive pigment the superficial concentration of zinc, encountered under similar exposure conditions, is appreciably smaller (100 mg m^{-2}). The phosphate content did not exceed 2400 mg m^{-2} . Larger amounts of iron were detected ($23\,000 \text{ mg m}^{-2}$).

CONCLUSIONS

The results of the salt spray test conducted with steel painted panels suggest that calcium acid phosphate is better than zinc phosphate and comparable to zinc tetroxychromate as an anticorrosive pigment. With zinc tetroxychromate it was also observed that the panel showed signs of localised attack. This was not observed when calcium acid phosphate was employed.

The polarisation curves show that the presence of calcium acid phosphate markedly decreased and sometimes completely inhibited the cathodic current for the oxygen reduction reaction compared with that for the blank solution. The anodic current for the iron oxidation was also diminished, compared with that for the blank solution, without producing any localised corrosion as in the case of zinc tetroxychromate.

From the foregoing discussion it can be seen that calcium acid phosphate performs in a similar manner to zinc tetroxychromate. However, it is neither toxic nor carcinogenic and it appears to stabilise the iron surfaces, thus impeding localised corrosion. Since calcium salts are generally cheaper than zinc salts it should be possible to produce calcium acid phosphate more cheaply than zinc phosphate.

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