THE INFLUENCE OF ZINC OXIDE ON THE ANTICORROSIVE BEHAVIOUR OF ECO – FRIENDLY PAINTS

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ABSTRACT

Zinc phosphate and related compounds have achieved wide application as suitable replacements for toxic and pollutant zinc chromates and lead oxides which were employed as anticorrosive pigments for paints. The behaviour of inorganic phosphates and tripolyphosphates may be improved by a suitable selection of complementary pigments.

The objective of this research work was to study the effect of substituting talc by zinc oxide in the pigment formula of anticorrosive alkyd paints. Different inorganic phosphates and tripolyphosphates were selected as active pigments. Paints with a pigment volume concentration/critical pigment volume concentration (PVC/CPVC) equal to 0.8 were formulated and their anticorrosive efficiency tested through accelerated and electrochemical tests.

Results showed that the incorporation of zinc oxide to the pigment formula improved corrosion resistance of painted steel, especially in the case of tripolyphosphates.

Key words: anticorrosive coatings, phosphates, tripolyphosphates, complementary pigments, zinc oxide.

INTRODUCTION

The long awaited reduction in the employment of classic active pigments (containing lead or hexavalent chromium) has induced an intense search for suitable alternative products to replace them /1-6/. Among these products, zinc phosphate and related compounds have achieved wide application. Particular attention has been paid to zinc phosphate, whose effectiveness had not been clearly established previously; however, more recent studies seemed to confirm the anticorrosive properties of zinc phosphate and related substances /2,4,5,7-9/. In accelerated tests, the behaviour of coatings pigmented with zinc phosphate may lead to disappointing results if paints are not formulated adequately /4, 5/, but these paints showed a good performance in outdoor long exposure tests /2/. Calcium acid phosphate was employed instead of zinc phosphate with better anticorrosive performance and lower environmental impact /10, 11/

The modification of zinc phosphate with suitable elements originated a new pigment series called the "second generation" phosphate pigments /4, 5/, while the "third generation" arose from substituting the phosphate anion by the tripolyphosphate one /12-16/. The replacement of phosphates by tripolyphosphates took place to meet the demands of high technology applications such as coil coatings. Both pigment series are claimed to have better anticorrosive behaviour than zinc phosphate itself. From previous studies, it was also noticed that the behaviour of inorganic phosphates may be improved by a suitable selection of complementary pigments /11, 17/.

The objective of this work was to study the effect of substituting talc by zinc oxide in the pigment formula of alkyd paints containing different anticorrosive pigments. Zinc phosphate, calcium acid phosphate, calcium tripolyphosphate and aluminium tripolyphosphate were selected as active pigments.

Zinc oxide was selected as the complementary pigment, taking into account some of its properties such as: its tendency to react with the acids that could be originated during the drying process of the alkyd film /18/, the capacity to regulate pH in film defects /19/, the ability to form inhibitive zinc soaps with reactive binders /20/, the possibility of polarising cathodic areas as calcium ions do /21/, etc. As a general rule, it was found that zinc oxide improved coating performance.

EXPERIMENTAL

Composition and manufacture of paints

The binder employed in this research was a medium oil alkyd containing 50 % linseed and tung oils, 30 % o-phthalic anhydride and 8 % pentaerythritol and glycerol. The solvent mixture was white spirit. It should be pointed out that solvent borne paints were chosen to evaluate pigment performance because their behaviour has been well documented for many years.

The anticorrosive pigment content was 30 % v/v, with respect to the total pigment content, and the PVC/CPVC ratio was 0.8. Four anticorrosive pigments were selected: zinc phosphate ($Zn_3(PO_4)_2$), calcium acid phosphate ($CaHPO_4$), calcium tripolyphosphate ($Ca_2NaP_3O_{10}$) and aluminium tripolyphosphate, $Al_5(P_3O_{10})_3$.

Titanium dioxide, talc and barium sulphate were also incorporated to complete one type of the pigment formula named as A. The replacement of talc by zinc oxide gave rise to a new pigment formula called, henceforth, B (Table 1). As a result, eight pigment mixtures were prepared and tested throughout this research work.

Table I

Pigment formula of tested paints expressed as percentage by volume

Solids	Pigment formula	
	A	B
Anticorrosive pigment	30.0	30.0
Barite	29.0	29.0
Titanium dioxide	12.0	12.0
Talc	29.0	-----
Zinc oxide	-----	29.0

The differences among the anticorrosive properties of the pigment mixtures were investigated by corrosion potential measurements and polarisation techniques (Tafel plots). The experiments were carried out employing a SAE 1010 steel electrode in pigment suspensions. The supporting electrolyte was 0.025 M sodium perchlorate in the case of corrosion potential measurements, while for polarisation studies the selected concentration was 0.5 M. Tafel plots were obtained from stirred, normal aerated suspensions, after 6 hours from the time the electrode was dipped into the pigment suspension.

Paint manufacture was carried out employing a ball mill with a 3.3 litres jar. Pigments were dispersed in the vehicle for 24 hours to achieve an acceptable dispersion degree /22/.

Paints were applied by brush on SAE 1010 steel panels (15.0x7.5x0.2 cm) up to a thickness of 75 ± 5 µm. The composition of SAE 1010 steel is, for the minor components, as follows: C: 0.12%, Si: 0.01%, Mn: 0.35%, S: 0.02%, P: 0.02%. Tested panels were previously sandblasted to Sa 2 1/2 (SIS 05 59 00, 20±4 µm maximum roughness), and then degreased with toluene. Painted panels were kept indoors for 7 days before being tested.

Accelerated and electrochemical tests performed on painted panels

Test panels were evaluated to establish the degrees of rusting (ASTM D 610) and blistering (ASTM D 714), after 700 hours of exposure to the salt spray cabinet (ASTM B 117). In all cases tests were carried out in triplicate, determining the mean value of the obtained results.

Another set of panels was placed in the humidity chamber (ASTM D 2247) at 100 % relative humidity and 38 ± 1°C, for 400 hours. The degrees of blistering and rusting were evaluated in accordance with the above mentioned standards.

The electrochemical cells to measure the variations of the corrosion potential of painted steel, as a function of time, were constructed by delimiting 3 cm^2 circular zones on the painted surface. An acrylic tube, 7 cm high, with one flat end was placed on the specimen and filled with the electrolyte (0.5 M sodium perchlorate solution). Measurements were taken during 1 month employing a saturated calomel electrode (SCE) as reference and a high impedance voltmeter.

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

The polarisation resistance of painted steel was determined, as a function of immersion time, by employing a cell with three electrodes. The reference electrode was SCE and the counterelectrode a platinum grid. The sweep

Table II

Corrosion potential and corrosion rate of steel in pigment suspensions

Inhibitive pigment	Pigment formula A			Pigment formula B		
	pH	Ecorr (mV)	Corrosion rate ($\mu A.cm^{-2}$)	pH	Ecorr (mV)	Corrosion rate ($\mu A.cm^{-2}$)
Zinc phosphate	7.03	-605	9.87	7.48	-560	4.95
Calcium acid phosphate	6.40	-560	5.00	7.77	-505	3.52
Calcium tripolyphosphate	7.02	-663	24.8	7.49	-480	2.39
Aluminium tripolyphosphate	6.26	-670	53.3	6.30	-517	2.83

Electrolyte: 0.025 M $NaClO_4$ for corrosion potential measurements and 0.5 M $NaClO_4$ for corrosion rate measurements. Corrosion rate of SAE 1010 steel in $NaClO_4$, 150 $\mu A.cm^{-2}$.

amplitude 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 352/252 software.

RESULTS AND DISCUSSION

Anticorrosive properties of pigments mixtures

The electrochemical behaviour of steel in pigment mixtures suspensions was assessed through corrosion potential measurements (Fig. 1) and Tafel plots (Fig. 2).

The corrosion potential of steel was displaced to more positive values when talc was replaced by zinc oxide in the pigment formula (Fig. 1). The corrosion potential vs time curve showed an ill defined peak pointing to the more positive potentials when talc was employed in the pigment mixture; but the corrosion potential rapidly moved towards more negative values. This fact may be attributed to some temporary degree of coverage of the electrode surface with siliceous materials and was not observed in the case of calcium tripolyphosphate. The coverage of steel surface by siliceous materials was previously studied by Bennet *et al.* /23/, who came to the conclusion that the diffusion coefficients of iron ions are highly reduced by these siliceous coatings.

From the examination of Tafel plots, it could be confirmed that zinc oxide displaced the corrosion potential of steel towards more positive values when added to the different pigment mixtures (Fig. 2, Table II). This fact indicates that a better anticorrosive protection was achieved in each case. The effect of zinc oxide was more pronounced in the case of tripolyphosphates than in the case of orthophosphates and it is more pronounced for calcium tripolyphosphate.

The examination of the cathodic branch of the Tafel plots (Fig. 2) showed that the oxygen reduction current diminished in the presence of inorganic phosphates and tripolyphosphates with respect to the blank (SAE 1010 steel in the supporting electrolyte). In some cases the oxygen current decreased ten times with respect to the blank. The oxygen reduction current in the supporting electrolyte was, on average, after 6 hours of exposure, 150 $\mu A.cm^{-2}$. There are no significant differences between the oxygen reduction current in the orthophosphate suspensions when talc is replaced by zinc oxide. However, the oxygen reduction current diminished appreciably in the

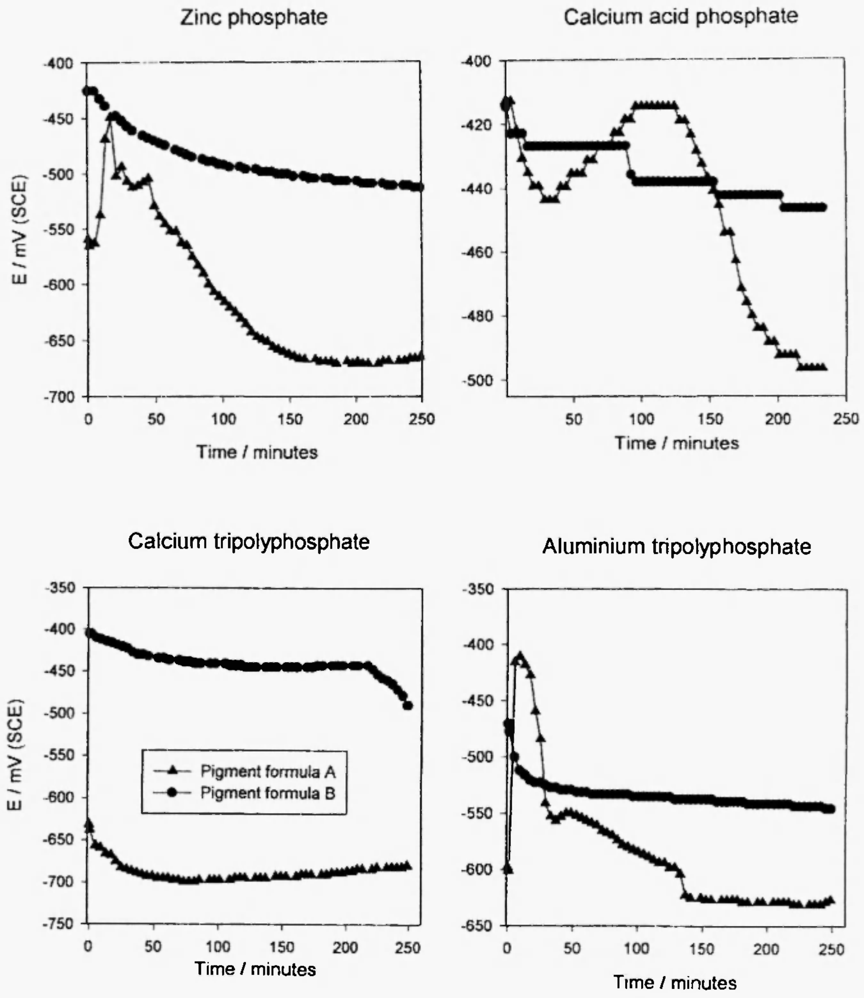
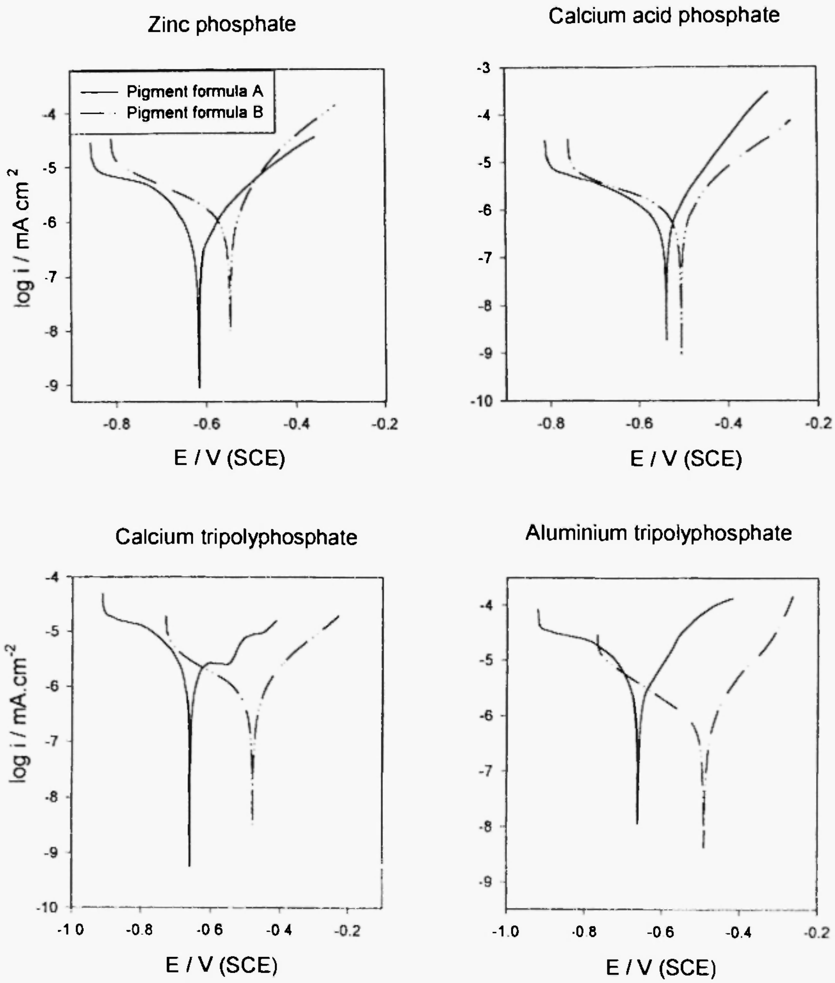


Fig. 1: Corrosion potential of sandblasted SAE 1010 steel panels (average surface roughness 20 ± 4 μm), as a function of the exposure time, in pigment mixtures suspensions. Supporting electrolyte: 0.025 M sodium perchlorate solution.

case of pigment mixtures containing the tripolyphosphates and zinc oxide in comparison with those containing talc. The cathodic reaction is more polarised than the anodic dissolution of steel when talc was replaced by zinc oxide. This may be attributed, probably, to a more effective electrode coverage with corrosion products /19, 24/.


Zinc phosphate

Calcium acid phosphate

Calcium tripolyphosphate

Aluminium tripolyphosphate

Fig. 2: Tafel plots of the SAE 1010 steel electrode, in pigment mixtures suspensions in 0.5 M sodium perchlorate solution. Scan rate 0.166 mV s^{-1}. Sweep amplitude ± 250 mV.

In the presence of talc, the anodic dissolution of steel was more polarised in the calcium tripolyphosphate suspension; the lowest polarisations were observed in the curve obtained with aluminium tripolyphosphate. The anodic reaction for calcium acid phosphate is slightly more polarised than for zinc phosphate, in the neighbourhood of the corrosion potential. As the overpotential increased, the anodic dissolution of steel, in the zinc phosphate suspension, proceeded at a higher rate.

The anodic dissolution of steel in tripolyphosphates suspensions is more polarised than in orthophosphate suspensions when talc is replaced by zinc oxide. Thus, tripolyphosphates in the presence of zinc oxide are better inhibitors of the anodic reaction than orthophosphates. Among all inhibitive pigments, the higher polarisations were detected for calcium tripolyphosphate and the pigment formula B. This inhibitor exhibited the lower corrosion rate (Table II).

In conclusion, zinc oxide had a striking influence on the anodic and on the cathodic behaviour of steel in pigment suspensions. The oxygen reduction current is reduced and the anodic reaction resulted polarised in a great extent. The effect is more striking for tripolyphosphates than for orthophosphates which are less influenced by the presence of zinc oxide. However, in all cases the corrosion rate was reduced in the presence of zinc oxide, being this effect more outstanding when tripolyphosphates were employed as anticorrosive pigments (Table II).

Accelerated tests

The results obtained in the salt spray test showed that the replacement of talc by zinc oxide was clearly advantageous. Paints containing talc in their composition attained a protection degree of 7-8 after 700 hours of exposure. At the same time many blisters of large or medium size developed on the painted surfaces (Table III). Panels coated with the paint containing aluminium tripolyphosphate failed after 24 hours (qualification 6) and were taken out from the salt spray cabinet. The replacement of talc by zinc oxide not only improved, in all cases, the anticorrosive behaviour of painted panels but also diminished the blistering of these paints. Zinc oxide was especially effective in the case of the paint containing aluminium tripolyphosphate, resulting in an improved corrosion resistance (qualification 8) without blistering.

As a general rule, it can be said that paints with zinc oxide, exposed to the humidity chamber, presented lower blister density as well as a reduction in blister size. The exception to this rule was the paint formulated with calcium tripolyphosphate as active pigment, which showed a 6MD degree with talc and 6D with zinc oxide (Table IV).

Table III

Rusting (ASTM D 610) and blistering (ASTM D 714) degrees of steel panels coated with alkyd anticorrosive paints, after 700 hours of salt spray test (ASTM B 117)

Pigment	Pigment formula A		Pigment formula B	
	Rusting	Blistering	Rusting	Blistering
Zinc phosphate	7	6D	8	6F
Calcium acid phosphate	8	4D	10	10
Calcium and sodium tripolyphosphate	8	2F	9	4F
Aluminium tripolyphosphate	-----	-----	8	10

----- Painted panels were taken out after 24 hours with rusting degree 6.

Table IV

Rusting (ASTM D 610) and blistering (ASTM D 714) degrees of steel panels coated with alkyd anticorrosive paints, after 400 hours in the humidity chamber (ASTM B 2247)

Pigment	Pigment formula A	Pigment formula B
Zinc phosphate	6MD	8M
Calcium acid phosphate	8D	10
Calcium and sodium tripolyphosphate	6MD	6D
Aluminium tripolyphosphate	8M	8F

Electrochemical tests.

As a general rule, the corrosion potential of painted steel showed more positive values when talc was replaced by zinc oxide (Fig. 3). This displacement (sometimes more than +300 mV) was significant in most cases except for aluminium tripolyphosphate, and was maintained at least during the first fortnight of immersion. This fact supports the improvement observed in the anticorrosive behaviour of paints in the salt spray cabinet. Zinc oxide

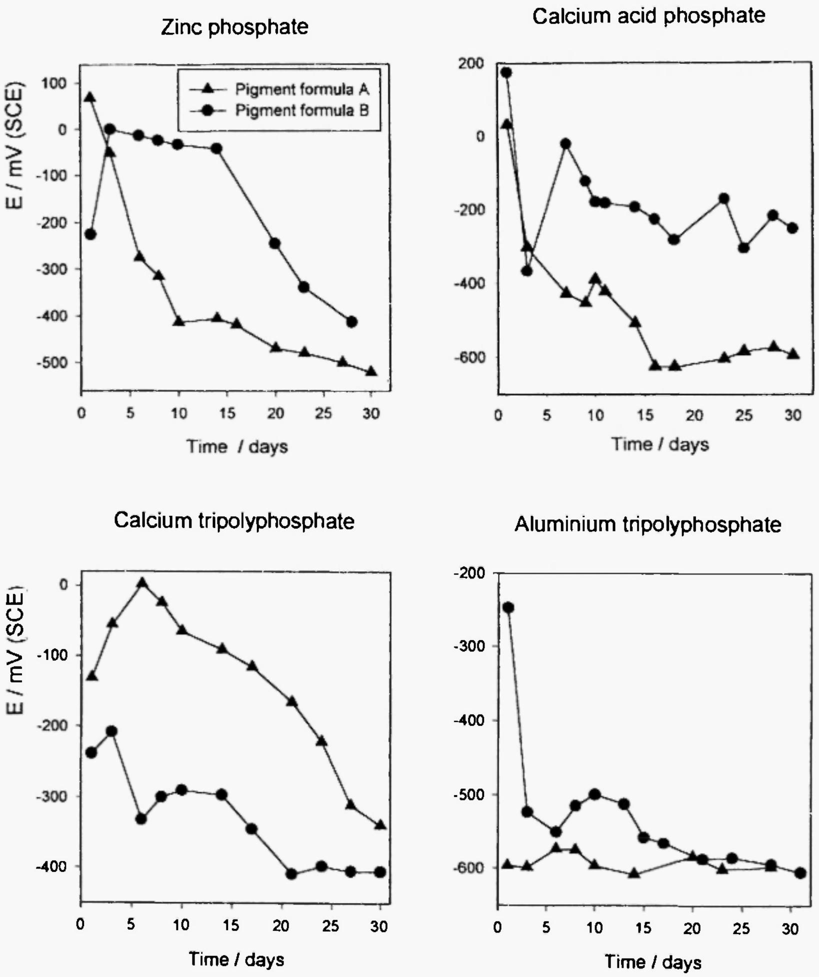


Fig. 3: Corrosion potential of steel coated with alkyd paints, as a function of the exposure time, in 0.5 M sodium perchlorate.

not only increased the pH of the medium (Table II), improving passivation /24/ but it also may precipitate a zinc oxide layer on the steel surface /10/.

The initial value of the ionic resistance of painted steel indicated that an acceptable barrier effect (Ri > 10^7 $\Omega.cm^2$) was achieved /25/, except for the coating formulated with aluminium tripolyphosphate. Paint formulated with aluminium tripolyphosphate and zinc oxide scarcely reached 10^6 $\Omega.cm^2$; but this value is appreciably higher than that obtained with talc and it is considered the minimum value desirable to achieve barrier properties. As a general rule, it can be stated that paints pigmented with the pigment formula B developed higher resistance values. As time passed, the differences between both types of pigment formula (A and B) may increase up to 4 orders of magnitude. In all cases, the incorporation of zinc oxide improved the sealing properties of the paints, which resulted in a better anticorrosive behaviour of tested paints in accelerated tests. The improvement was notable in the case of aluminium tripolyphosphate. The only paints that maintained the initial barrier effect were those pigmented with the orthophosphates and zinc oxide. On the contrary, paints containing talc lost their barrier properties after the first day of immersion (Fig. 4).

The ionic resistance of paints formulated with tripolyphosphates was lower than the ionic resistance of paints containing orthophosphates (Fig. 4). The initial barrier effect was lost after two days of immersion. The presence of zinc oxide improved the barrier properties of the coating, but they never matched the values obtained with orthophosphates. This behaviour may be attributed to the higher solubility of tripolyphosphates with respect to orthophosphates /9, 26/.

The polarisation resistance of paints formulated with pigment formula B and the inhibitors zinc phosphate and calcium acid phosphate could not be measured during the test period due to the high ionic resistance of the film (Fig. 5). In this case a linear response, indicating ohmic control, is likely to be obtained and the current involved in the experiment may be small and difficult to measure with accuracy. The polarisation resistance of steel coated with paints formulated with the orthophosphates and talc decreased continuously as time elapsed because it followed the ionic resistance of the film. However, the polarisation resistance was higher than the ohmic one due to the inhibitive action of the pigment /25/.

In the case of tripolyphosphates, the high ionic resistance diminished after 10 days of immersion for calcium tripolyphosphate and after 1 day for the aluminium one. The polarisation resistance may greatly exceed the ionic

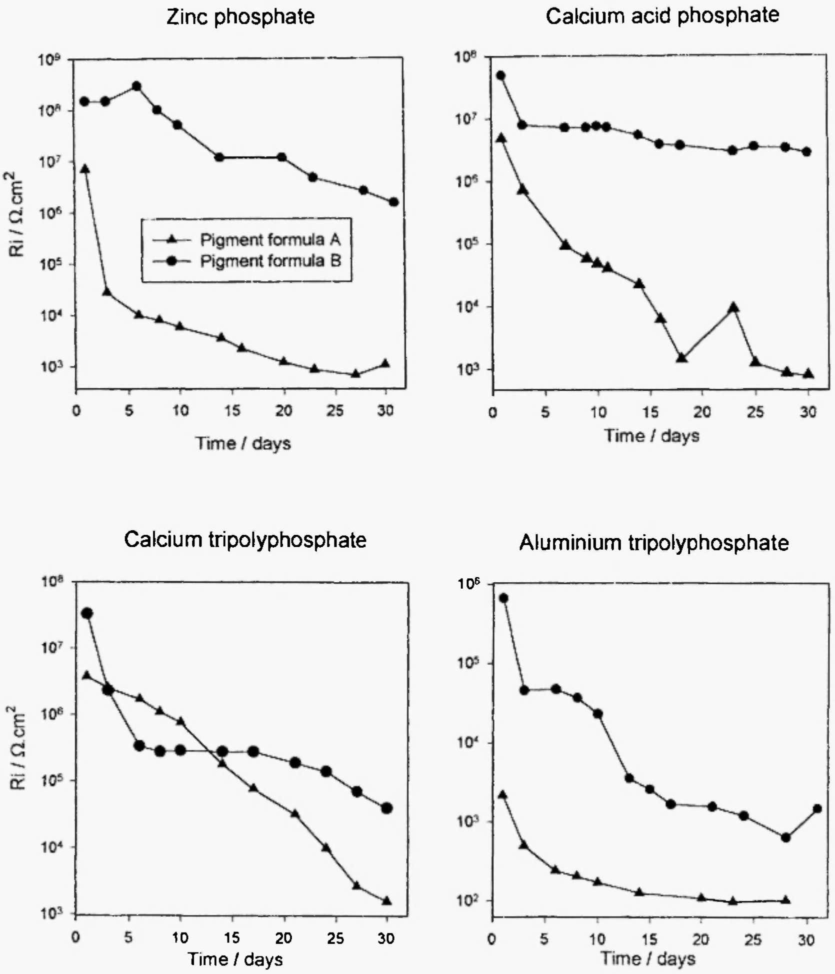


Fig. 4: Ionic resistance of steel coated with alkyd paints, as a function of the exposure time, in 0.5 M sodium perchlorate.

resistance (more than 20 times); thus indicating an active inhibition of steel corrosion /25/. The presence of zinc oxide in the pigment formula markedly increased the polarisation resistance, thus improving corrosion resistance of painted specimens (Fig. 5).

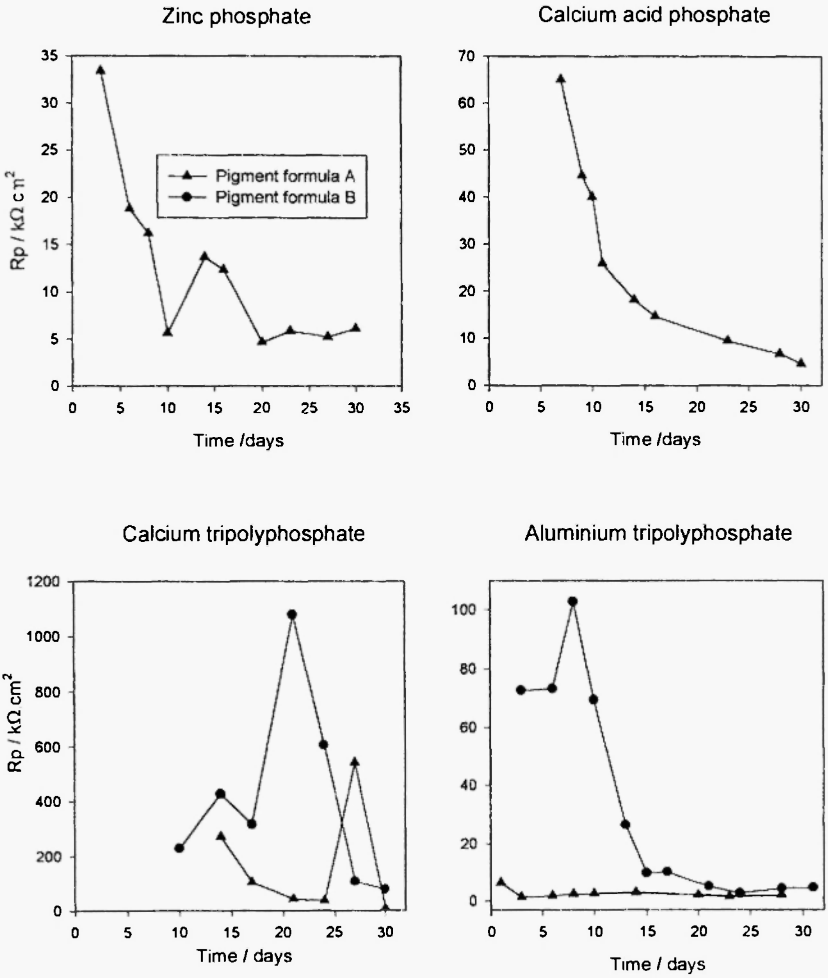


Fig. 5: Polarisation resistance of steel coated with alkyd paints, as a function of the exposure time, in 0.5 M sodium perchlorate.

CONCLUSIONS

- Both phosphates and tripolyphosphates proved to be adequate active pigments to formulate anticorrosive paints to protect steel.
- The anticorrosive properties of the pigments may be enhanced by a careful selection of complementary pigments.
- Zinc oxide shifted the corrosion potential of painted specimens to more positive values, indicating a better protection of the steel substrate.
- Zinc oxide was found to improve the anticorrosive performance of paints containing phosphates and tripolyphosphates. It has a striking influence on the anodic and on the cathodic behaviour of steel in pigment suspensions. In all cases the corrosion rate was reduced by the presence of zinc oxide, this effect being more noticeable when tripolyphosphates were employed as anticorrosive pigments.
- Zinc oxide improved the barrier properties of the coatings, especially those formulated with orthophosphates.
- The presence of zinc oxide in the pigment formula markedly increased the polarisation resistance, thus improving corrosion resistance of painted specimens.
- The protection is afforded by a barrier mechanism followed by the inhibition of cathodic and/or anodic reactions when the barrier properties are lost.
- The results obtained in accelerated tests (salt spray and humidity chamber tests) agree with those from electrochemical measurements. Zinc oxide improved anticorrosive performance of paints and diminished their tendency to blistering.

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