Three generations of inorganic phosphates in solvent and water-borne paints: A synergism case

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Abstract

This research work is intended to compare the anti-corrosive properties of three generations of inorganic phosphate pigments in solvent-based paints and in water-borne ones, both of the epoxy type. The anti-corrosive properties of phosphate pigments were assessed by means of electrochemical techniques (corrosion potential measurements, polarisation tests, etc.), employing a steel electrode dipped into pigments suspensions. The behaviour of these pigments in anti-corrosive paints, formulated with different binders, have been studied by accelerated (salt spray cabinet and humidity chamber) and electrochemical tests (corrosion potential and ionic resistance measurements).

Accelerated and electrochemical tests allowed to differentiate the anti-corrosive performance of the three phosphates studied in this research. These test are also able to detect and characterise possible synergism between the water-borne resin and the pigments.
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Keywords: Corrosion protection; Steel passivation; Coatings; Phosphate pigments; Synergism; Protective layer

1. Introduction

From 1970 on, two major goals were achieved in the field of paint technology: the replacement of toxic inhibitive pigments and the progressive elimination of solvents in paint formulations to fit VOC's regulations.

Traditional anti-corrosive paints contain lead or hexavalent chromium compounds as active pigments, which contaminate the environment and, at the same time, represent a risk to human health. Many compounds have been suggested as possible replacements for chromates and lead compounds but zinc phosphate and related substances became the leading substitutes for toxic inhibitors. Three generations of phosphates were introduced in the market, being zinc phosphate the precursor [1–10]. The second generation was developed by performing suitable modifica-

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tions in the zinc phosphate particle [7–14]. Finally, the third generation was designed to meet high technological applications and was obtained changing the orthophosphate anion by the tripolyphosphate one [15–25].

As a general rule, it can be said that the protective action of phosphates is due to the formation of an iron oxyhydroxides film, on the steel substrate, which is non expansive in nature. It also involves the polarisation of cathodic areas by the precipitation of sparingly soluble salts which adhere to the surface [2,26,27].

Due to the imposition of the increased legislative restrictions on the emission of the organic materials to the atmosphere, water-borne coatings are finding more and more importance for both do-it-yourself and industrial coatings applications. Water, as a solvent, has two main advantages because it is non-toxic and non-flammable. Water-borne systems present a range of characteristic differences and, in some cases, difficulties not exhibited by solvent-borne paints [28–32]. It was stated everywhere that water-borne paints are less resistant to the corrosion process generated by water, ions and oxygen permeation and prone to biological attack [29,33–36]. They also exhibit "flash rusting" during solvent evaporation which finally affects the appearance of the coating [33,36,37].

The objective of this research was to compare the anticorrosive performance of solvent and water-borne paints, formulated with three anti-corrosive pigments, belonging each one to a different generation of phosphate pigments. The anti-corrosive behaviour of the paints was evaluated through accelerated and electrochemical tests.

2. Experimental

2.1. Pigment characterisation

Three different pigments were selected to carry out this research: zinc phosphate (Pigment 1), zinc molybdenum phosphate (Pigment 2) and zinc tripolyphosphate (Pigment 3). The two former pigments were commercially available; the last one was prepared in the laboratory, by precipitation from the corresponding soluble salts [25].

Pigments composition was established employing current analytical techniques. Physicochemical prop-

erties of pigments, relevant to paint technology, such as density (ASTM D 1475) and oil absorption (ASTM D 281), were measured, according to standardised procedures, in order to sketch a correct formulation of the paint. The pH and the ionic composition of the aqueous saturated solution were also determined.

The inhibitive properties of the anticorrosive pigments were evaluated by means of electrochemical techniques, employing SAE 1010 steel electrodes with low surface roughness (mean peak-to-valley height 1.40 μm), in pigments suspensions. The corrosion potential was monitored as a function of time, in the corresponding pigment suspension, against a saturated calomel electrode (SCE) as reference and 0.025 M sodium perchlorate as supporting electrolyte.

Steel corrosion rates, in pigments suspensions in 0.5 M sodium perchlorate, were obtained from polarisation resistance measurements. A SCE and a platinum grid were used as reference and counter electrodes, respectively. The swept amplitude was ± 20 mV from the open circuit potential and the scan rate 0.250 mV s^{-1}. Measurements were carried out with a Potentiostat/Galvanostat EG&G PAR Model 273A plus SOFTCORR 352 software. Anodic and cathodic polarisation curves, in a wider potential range, were also obtained employing a similar electrolytic cell. The electrochemical experiments were repeated adding to the electrolyte solution the resin and the hardener used to formulate the water-borne paints. These two components were dosed in the same proportion as in the paint (resin/hardener ratio: 1.0/1.2 parts by weight).

2.2. Paints composition, manufacture and application

Two different epoxy paints were formulated to carry out this research; one of them was a solvent-borne paint and the other a water-borne one.

The resin employed to formulate solvent-borne paints was a bisphenol epoxy-polyamide resin (1:1 ratio v/v). The corresponding solvent mixture was composed of xylene/methyl isobutyl ketone/butyl cellosolve (13/45/42%, by weight). The PVC/CPVC relationship was 0.8 as suggested elsewhere [9,10]. The anticorrosive pigment load was 30% v/v of the total pigment content; as suggested in the literature for phosphate pigments [6,9,10]. Titanium dioxide, barium sulphate and talc complete the pigment

Table 1
Paints solids composition (% volume of solids)

Components	Solvent-borne paint	Water-borne paint
Anti-corrosive pigment	12.6	5.8
Titanium dioxide	4.8	3.5
Barium sulphate	12.2	3.7
Talc	12.2	3.4
Mica	–	3.0
Epoxy resin/polyamide resin (1/1 ratio)	58.2	–
Hardener/resin (1.2/1 ratio)	–	78.6
Additives	–	2.0
Anti-corrosive pigment/total pigment (v/v)	30	30

formula, which may be seen in Table 1. All pigments were dispersed 24 h in the vehicle, employing a ball mill, to achieve an acceptable dispersion degree [38].

An epoxy resin, based on a mix of bisphenol A and bisphenol F, was chosen to formulate the water-borne paints; the curing agent (hardener), which also acts as emulsifier, was a modified polyamidoamine with 50% of solids. The resin/hardener ratio was 1.0/1.2 parts by weight. Neutral de-mineralized water was employed as paint solvent.

The anti-corrosive pigment content was the same employed for the solvent borne paint but mica was also incorporated as complementary pigment in order to enhance the barrier properties of the coating and reduce the degree of "flash rusting" [37]. The selected PVC was 20% to produce a more impervious coating.

Paints manufacture was carried out employing a high-speed disperser equipment; preliminary tests showed the advantage of incorporating the pigment into the hardener instead of mixing it with the resin. Water was added firstly due to the relatively high viscosity of the hardener, then pigments were incorporated in accordance with their increasing oil absorption. Mica was added at the end of this process to avoid the break-up of laminar particles.

SAE 1010 steel panels (15.0 cm × 7.5 cm × 0.2 cm) were sandblasted to Sa 21/2 (SIS 055900), degreased with toluene and then coated with the paints described in Table 1, by brushing, up to a thickness of 80 ± 5 μm. Painted panels were kept indoors for 14 days before testing.

2.3. The performance of anti-corrosive paints through accelerated and electrochemical tests

For each type of paint, a set of 3 panels was placed in the salt spray chamber (ASTM B-117). Rusting (ASTM D-610) and blistering (ASTM D-714) degrees were evaluated after 2000 and 2400 h of exposure. Another set of panels was placed in the humidity chamber, at 38 ± 1 °C (ASTM D 2247), for 860 h, to evaluate blistering according to the above mentioned standard specifications.

The electrochemical cells employed to evaluate the anti-corrosive performance of painted steel were constructed by delimiting 3 cm^2 circular zones on the painted surface. An acrylic tube (7.0 cm high) was placed on the specimen and filled with the electrolyte (0.5 M sodium perchlorate solution). The corrosion potential of coated steel was measured employing a calomel electrode (SCE) as reference and a high impedance voltmeter. The resistance between the coated steel substrate and a platinum electrode was also measured employing an ATI Orion, model 170, conductivity meter, at 1000 Hz.

3. Results and discussion

3.1. Pigments characterisation

The composition of commercial pigments, obtained from chemical analysis of the corresponding samples, coincided with specifications found in technical sheets [39,40]. The main component of these pigments was zinc phosphate. Pigment 1 had the stoichiometry of zinc phosphate ($Zn_3(PO_4)_2 \cdot 2H_2O$): 45% of PO_4^{3-} and 46.5% of Zn^{2+}. The rest of the pigment formula, as in all cases; was constituted by water molecules and its percentage determined by heating at different temperatures. Pigment 2 contained 0.50% of $ZnMoO_4$, 35.7% of PO_4^{3-} and 47.6% of Zn^{2+}. As there was an excess of Zn^{2+} and no other species were detected, it was concluded that its composition was: 86.1% of zinc phosphate ($Zn_3(PO_4)_2 \cdot 4H_2O$) and 13.4% of zinc oxide. Both phosphates were micronized (average particle size 1–5 μm). Zinc molybdenum phosphate belongs to the so called "second generation" of phosphate pigments because it was modified by adding 0.50% of $ZnMoO_4$

and zinc oxide. It was claimed that zinc molybdenum phosphate has equal or superior anti-corrosive behaviour than zinc chromate [6,9–12], being the active inhibitive species the molybdate anion. The action of molybdenum was found to be the same either it was added directly to the electrolyte solution or to the metal alloy. It was found that molybdate anion added to a hydrochloric solution can help re-passivation of stainless steel undergoing stress corrosion cracking by depositing itself on the bare metal surface [41]. However, some authors [42] did not found molybdenum in the passive layer, but demonstrated that it affected the composition of the inner chromium oxide layer in stainless steels. Qvarfort [43], on the contrary, detected the presence of a passivating film on steels which dissolved later as a consequence of the corrosion process, being molybdenum compounds located in the porous layer of corrosion products. Hugot-Le Goff and co-workers [44–47] studied iron and several iron alloys containing molybdenum and established that steel protection was ensured, before pitting, by a very thin film of ferrous molybdate. The effect of corrosion was to reduce the thickness of this film and passivity breakdown was associated with the reduction of molybdenum from the +6 state to the +4 state; when all Mo(VI) species were reduced, pitting corrosion starts. So, it was concluded that molybdate anion added to zinc phosphate can help to passivate the steel surface.

The third pigment, zinc tripolyphosphate, was prepared in the laboratory, as it was said previously, and its composition was found to be 47.6% of PO_4^{3-}, 24.4% of Zn^{2+}, 2.1% of Na^+. According to this results, the stoichiometry of zinc tripolyphosphate was found to be $Zn_2NaP_3O_{10} \cdot 5H_2O$.

The phosphate content in the saturated solution of pigments 1 and 2 was found to be lower than 1.5 ppm and the zinc content did not exceed 4.3 ppm, as it could be expected to occur with orthophosphates (Table 2). The pH of the saturated aqueous solution of zinc molybdenum phosphate (Pigment 2) and the soluble Zn^{2+} concentration is consistent with the presence of zinc oxide in the pigment formula. In this way, zinc oxide may improve steel passivation, leading to better anticorrosive performance by two different mechanisms: the increased pH of the electrolyte solution and the polarization of cathodic areas [2,48,49]. The solubility increased in the case of

Table 2
Composition and pH of the saturated solution of the anti-corrosive pigments

Pigment	Composition of the saturated solution		
	Zn^{+2} (ppm)	PO_4^{3-} (ppm)	pH
1	2.0	<1.5	6.68
2	4.3	<0.1	8.10
3	8.92	5.47	5.75

1: zinc phosphate; 2: zinc molybdenum phosphate; 3: zinc tripoly-phosphate.

zinc tripolyphosphate (Pigment 3); thus, the "third generation" phosphate pigment is characterised by leaching higher amount of passivating species into solution.

Electrochemical tests revealed that all pigments protected steel against corrosion. Steel corrosion potential, in every pigment suspension, was more positive than the corrosion potential of steel in the supporting electrolyte (Fig. 1). Zinc phosphate and zinc molybdenum phosphate shifted the corrosion potential towards more positive values than zinc tripolyphosphate did. Zinc tripolyphosphate behave as a classical anti-corrosive pigment did. So, it exhibited a broad peak pointing to more positive values which began to decrease steadily beyond 150 min of exposure (Fig. 1). After 24 h of exposure, the
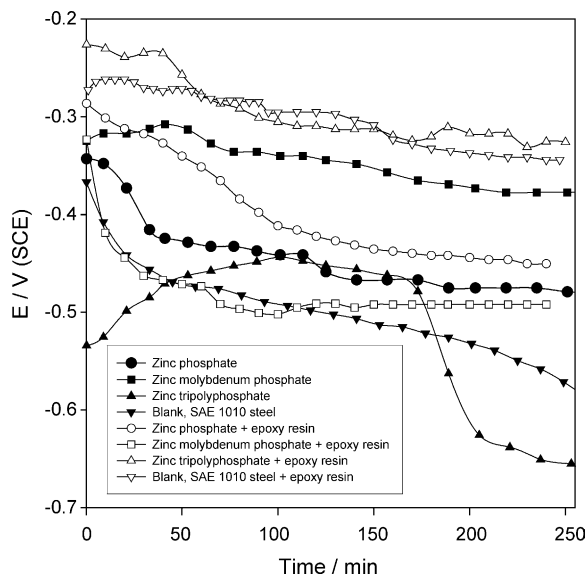

Fig. 1. Corrosion potential of steel in pigments and pigments + water-borne resin suspensions. Electrolyte: 0.5 M NaClO₄.

corrosion potential of steel in contact with zinc phosphate was measured and found to be −0.690 V, that of zinc molybdenum phosphate was equal to −0.600 V and −0.622 V was the value attained by the steel panel in zinc tripolyphosphate suspension. However, no signs of corrosion were detected in any case. This result and the corrosion potential values measured after 24 h of exposure confirmed that corrosion products were a certain type of iron oxyhydroxide layer, as it was stated in the literature [26,27]. The protective layer was studied by scanning electron microscopy (SEM) and its composition determined by EDAX.

As it could be expected, protective films formed on steel strongly depended on the type of pigment. Zinc phosphate generated a uniform film on steel, basically composed of iron oxide (Fig. 2). In a foreground, a
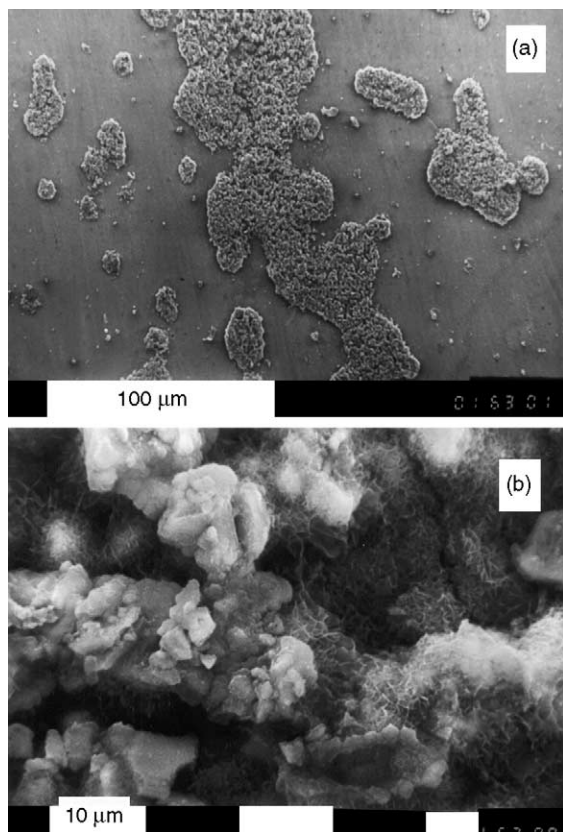

Fig. 2. SEM microphotograph of the steel surface after being in contact (24 h) with zinc phosphate in suspension in 0.025 M NaClO₄. (a) Panoramic view (magnification 50×); (b) oxide formations (magnification 2500×).
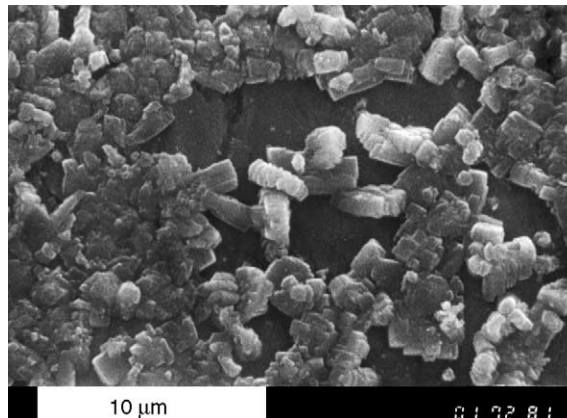

Fig. 3. SEM microphotograph of the steel surface after being in contact (24 h) with zinc molybdenum phosphate in suspension in 0.025 M NaClO₄ (magnification 5000×).

different structure was observed which average composition was: P: 27.85%, Fe: 6.78% and Zn: 65.37%. In a second plane filament-like particles were detected, which contained higher amounts of iron and had the following average composition: P: 6.60%, Fe: 57.05% and Zn: 36.35%. This fact led to think that this particle corresponded to zinc oxide and an iron oxide, of early formation, which could be then phosphatised. The precipitation of zinc oxide is also desirable because it polarises cathodic areas, diminishing corrosion rates [2].

A continuous film developed on the steel surface in contact with zinc molybdenum phosphate, covering it all (Fig. 3). At higher magnifications, small crystals of a compound rich in iron was observed whose composition was: P: 13.40%, Fe: 69.71% and Zn: 16.89%. Molybdenum compounds were not detected in the protective film.

As in the other cases, zinc tripolyphosphate induced the formation of an oxide layer which covered the whole metal surface (Fig. 4). The composition of the layer was: P: 5.82%, Fe: 92.27% and Zn: 1.91%. It is believed that oxides were stabilised by the presence of P and Zn, avoiding the growth of globular expansive iron oxides. Globular white formations were enriched in phosphorous and zinc, being the average composition: P: 21.23%, Fe: 67.79% and Zn 10.98%. These formations are thought to be useful to plug the pores opened in the oxide layer.
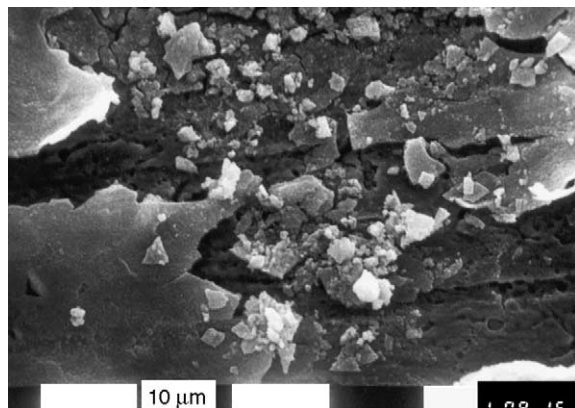
Fig. 4. SEM microphotograph of the steel surface after being in contact (24 h) with zinc tripolyphosphate in suspension in 0.025 M NaClO$_4$ (magnification 500×).

Fig. 5. (a) SEM microphotograph of the steel surface covered by the water-borne resin (magnification 600×); (b) SEM microphotograph of the steel surface covered by the oxide layer grown in 0.025 M NaClO$_4$ (magnification 350×). Exposure time: 24 h.

The corrosion potential of steel in the presence of the water-soluble resin was, as a general rule, displaced towards more positive values. The only exception was zinc molybdenum phosphate; however, in spite of the negative shifting of the corrosion potential, no signs of corrosion were observed on the metal surface. The most striking effect was observed with zinc tripolyphosphate whose inhibitive properties seemed to be highly improved, as if there was a synergism between the pigment and the resin. This effect is less pronounced in the case of zinc phosphate. After 24 h of exposure, the corrosion potential of steel panel in contact with zinc phosphate was −0.548 V, that of zinc molybdenum phosphate −0.519 V, being the most positive the value encountered for zinc tripolyphosphate, −0.410 V. The presence of the resin clearly improved the anticorrosive behaviour of the pigments. The corrosion potential of steel in the presence of the different pigments was displaced towards more negative values with respect to the curve obtained with the resin alone. The presence of this resin had two important effects: the resin by itself passivated the steel substrate and generated a synergism with each pigment. The shifting in the potential values is interpreted as a competence between the resin molecules and oxide particles for the active sites of the steel surface. The examination of the steel surface by SEM showed that the resin deposited onto the metal surface refilling all the cavities that appeared on it (Fig. 5a), thus preventing the formation of expansive iron oxides which may grow in the electrolyte solution, in the absence of the resin (Fig. 5b).
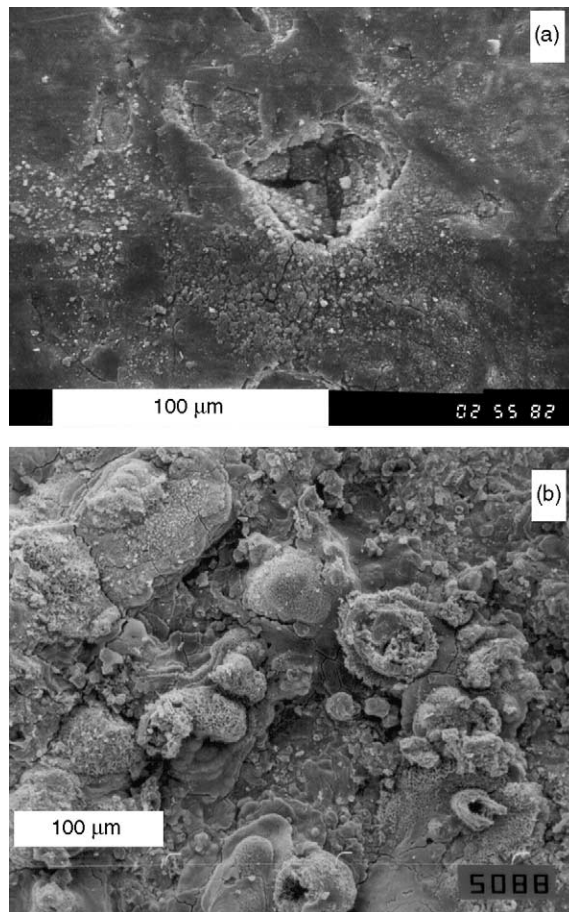
Steel corrosion rate diminished in the presence of the different phosphates (Table 3), indicating that they are able to protect steel. Zinc molybdenum phosphate is the best inhibitor while zinc phosphate showed the poorest behaviour. The presence of the epoxy water-soluble resin affected the behaviour of the pigments being zinc tripolyphosphate the best inhibitor of the series. The epoxy resin also reduced the corrosion rate of steel in the supporting electrolyte.

The analysis of the anodic polarisation curves revealed that the lowest critical current density to achieve passivation corresponded to zinc molybde-

Table 3
SAE 1010 steel corrosion rate in pigments suspensions after 24 h of exposure

Pigment	Corrosion rate ($\mu A\ cm^{-2}$)	
	Without resin	With epoxy resin
1	6.47	5.70
2	1.45	1.50
3	3.4	0.41
Blank, SAE 1010 steel in 0.025 M NaClO$_4$	11.4	6.8

1: zinc phosphate; 2: zinc molybdenum phosphate; 3: zinc tripolyphosphate.

num phosphate and to zinc tripolyphosphate. The lowest current density in the passive zone corresponded to zinc tripolyphosphate (Fig. 6a). After 24 h, the oxidation of the steel electrode in contact with the zinc phosphate suspension was less polarised and the current in the passive zone increased notably. Currently in the passive zone also increased in the presence of zinc molybdenum phosphate. In change, the electrochemical reaction was more polarised in the presence of zinc tripolyphosphate (Fig. 6b). The inhibitive action of the three pigments was clearly appreciated in both figures because the curve of the blank exhibited higher peak currents and higher currents in the passive zone.

The i–E anodic profile was substantially modified when the epoxy resin was added to the pigment suspension. Except for zinc phosphate, it can be said that the electrochemical reaction is much more polarised and the oxidation peaks appeared at more positive potentials. It is noticeable the influence of the resin on the dissolution of SAE 1010 steel which resulted more polarised (Fig. 7a). This fact points out that the resin by itself restrains steel dissolution.

After 6 h of exposure, the i–E profile, in the case of zinc phosphate, showed a linear increase, from the vicinity of the corrosion potential, as if there existed an ohmic control for steel dissolution. The peaks appeared to be displaced to more positive potentials revealing that the electrochemical reaction was more polarised in the presence of the resin. The observed current densities were still high in spite of the polarisation of the anodic reaction. In the other cases, the anodic reaction was almost inhibited in a wide potential interval. The anodic reaction, in the presence of zinc molybdenum phosphate, was greatly inhibited in the whole potential range scanned in this experiment (Fig. 7a).
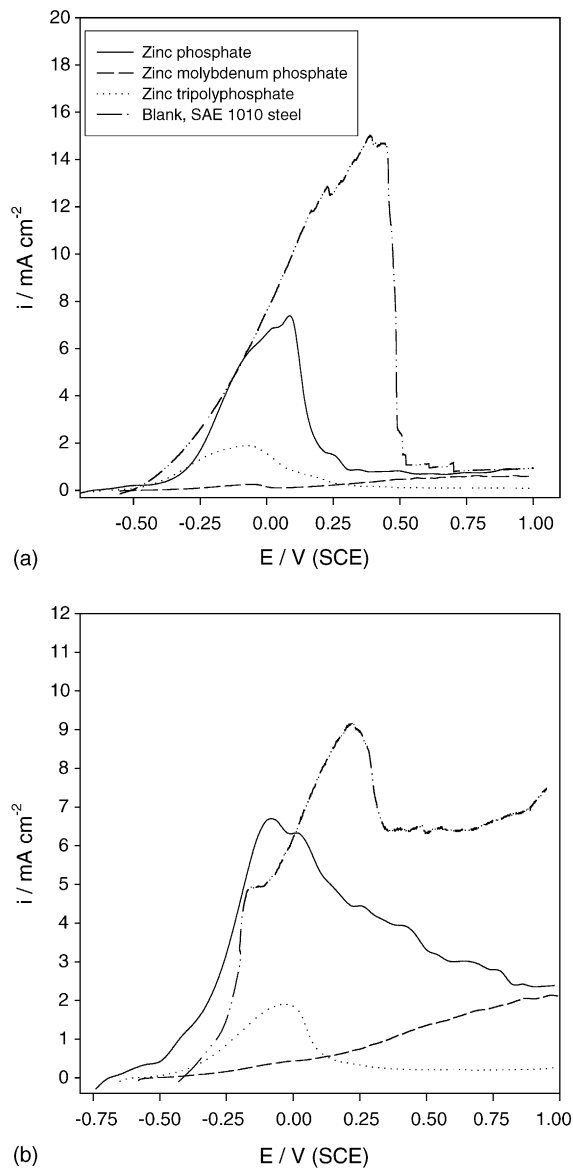

Fig. 6. Anodic polarisation curves of the SAE 1010 steel electrode in the pigments suspensions after: (a) 6 h and (b) 24 h of exposure. Electrolyte: 0.5 M NaClO$_4$. Scan rate: 3 mV s^{-1}.

The electrochemical reaction was activated after 24 h of exposure of the steel electrode to the anticorrosive pigment + resin suspension. This activation of the oxidation process was perceivable through the increase of the peak currents for the three pigments tested in this research. However, it must be pointed out that the anodic reaction remained polarised in the
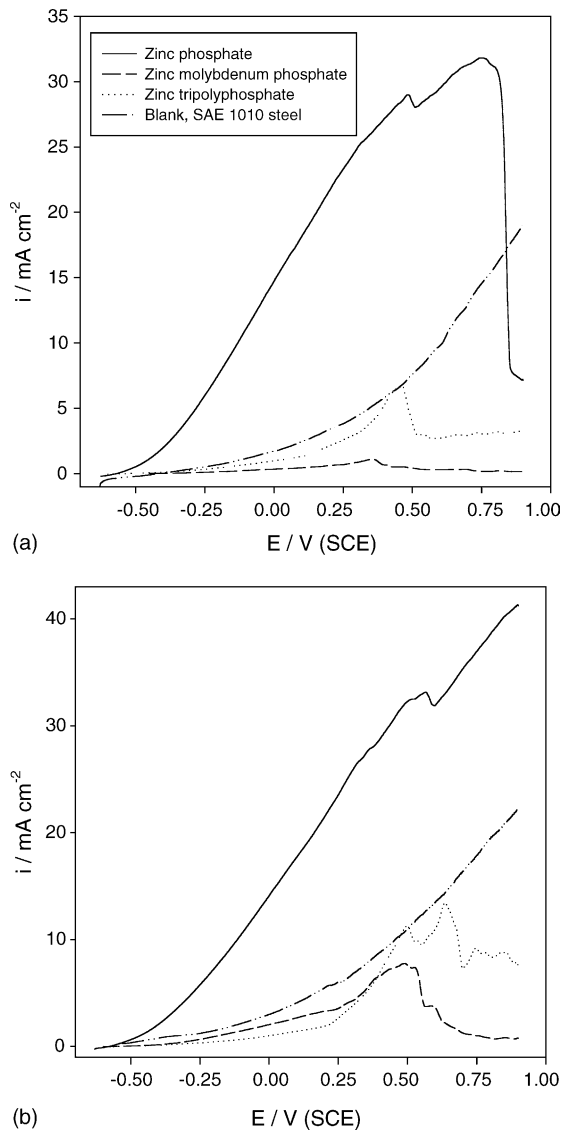
Fig. 7. Anodic polarisation curves of the SAE 1010 steel electrode in the pigments + water-borne resin suspensions after: (a) 6 h and (b) 24 h of exposure. Electrolyte: 0.5 M $NaClO_4$. Scan rate: 3 mV s^{-1}.

evolution, which could not be attributed only to oxygen reduction; it is clear that oxides reduction was superimposed to the oxygen discharge (Fig. 8a). This cathodic current diminished in the presence of different phosphates, being this diminution due either to the inhibition of oxide formation by the action of the pigments or to the blocking of active sites for oxygen reduction. After 24 h of exposure, no significant
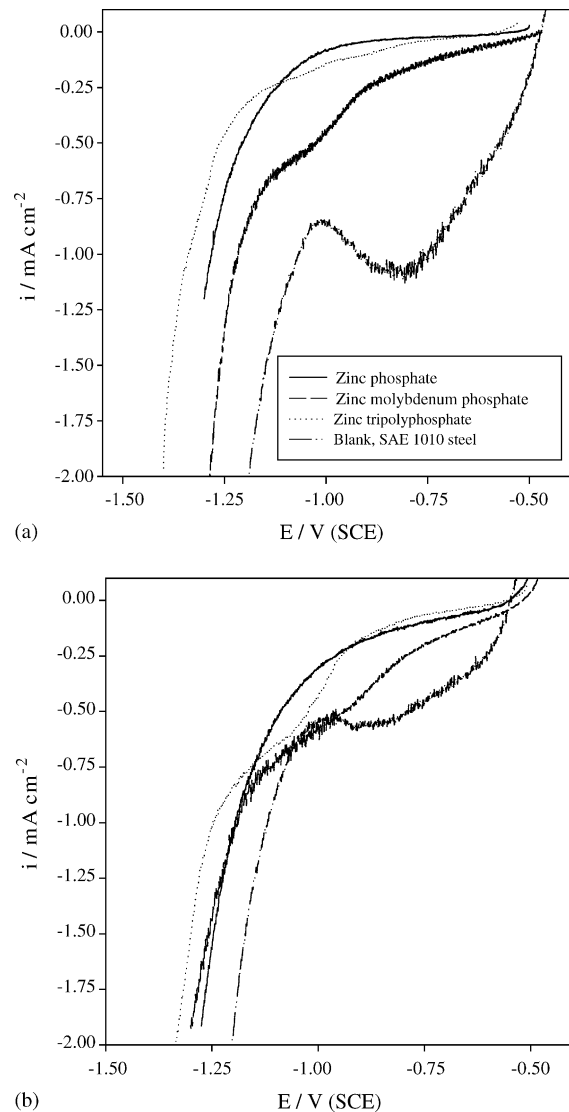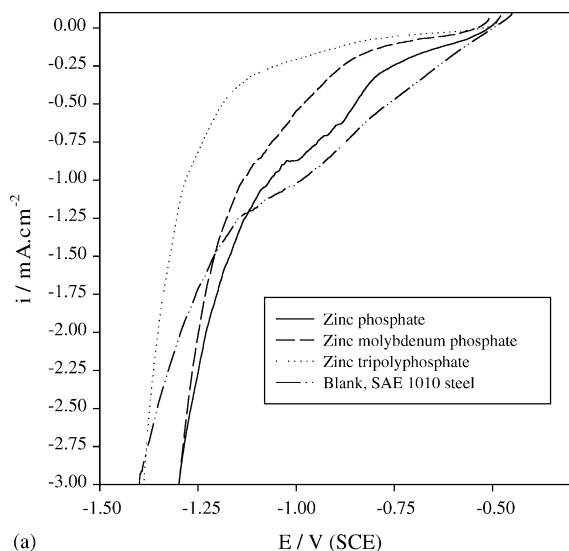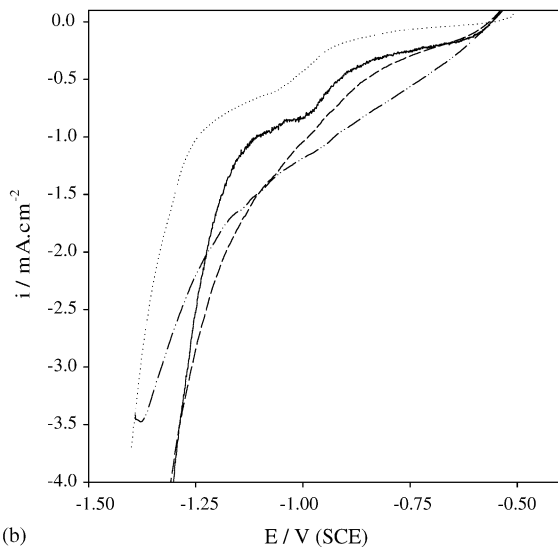

Fig. 8. Cathodic polarisation curves of the SAE 1010 steel electrode in the pigments suspensions after: (a) 6 h and (b) 24 h of exposure. Electrolyte: 0.5 M $NaClO_4$. Scan rate: 3 mV s^{-1}.

neighbourhood of the corrosion potential and the peak current displaced to very positive values (Fig. 7b). The oxidation of the steel electrode, in the absence of anti-corrosive pigments, was also polarised and did not change significantly after 24 h of exposure.

The examination of the cathodic curve of steel in the supporting electrolyte solution revealed the presence of a high current, previous to hydrogen

changes were observed except that some curves exhibited lower currents (Fig. 8b). The incorporation of the water-soluble resin did not modify this behaviour except that, in some cases, current was lower. This is true for steel in the supporting electrolyte, the reaction seemed to be more polarised and this behaviour may be attributable to the interaction between the resin and the electrode

(a)

(b)

Fig. 9. Cathodic polarisation curves of the SAE 1010 steel electrode in the pigments + water-borne resin suspensions after: (a) 6 h and (b) 24 h of exposure. Electrolyte: 0.5 M NaClO$_4$. Scan rate: 3 mV s^{-1}.

Table 4
Rusting degree (ASTM D 610) of painted panels in the salt spray chamber (ASTM B 117) and blistering degree (ASTM D 714) in the humidity chamber (ASTM D 2247)

Paints	Salt spray cabinet		Humidity chamber
	2100 h	2400 h	860 h
1A	6	–	8 M
2A	10	10	10
3A	8	7	10
1B	10	10	8 F
2B	10	10	8 F
3B	10	10	8 M

The paints are named with a number referring to the pigment and a letter referring to the binder. The letter A will be for solvent paints while the letter B for water-borne paints. 1: zinc phosphate; 2: zinc molybdenum phosphate; 3: zinc tripolyphosphate. ASTM D 610: the degrees of rusting on painted steel surface are between 10 and 0. 10 is for no rusting, 8 for less than 0.1% and 6 for less than 1% of the surface rusted. The panels were taken out when the qualification was 6 or lesser. ASTM D 714: the numerical scale is from 10 to 0, in which No. 10 represents no blistering and blistering standard No. 8 represents the smallest size blister easily see by the unaided eye. The reference standards in frequency are: M, medium and F, few.

(Fig. 9a and b). The lowest currents were observed for zinc tripolyphosphate.

3.2. The performance of anticorrosive paints through accelerated and electrochemical tests

The best anti-corrosive behaviour in the salt spray test was achieved by water-borne paints, the qualification was 10 for all the pigments studied in this research (Table 4). These paints did not show corrosion spots even after 2400 h of exposure. This behaviour could be explained in terms of the interaction between the resin and the substrate which was modified by phosphate pigments, as stated before.

In the case of the solvent borne paints the worst anti-corrosive behaviour was observed for zinc phosphate, as it could be expected from the foregoing discussion of the electrochemical tests. The paint pigmented with this pigment developed an important corrosion process after 2100 h in such a way that it had to be taken out from the salt spray chamber. Zinc molybdenum phosphate (pigment 2) had a very good performance in both binders, no signs of corrosion were observed on the painted panels after 2400 h of exposure. After 2100 h of essay the solvent borne paint containing zinc tripolyphosphate (paint 3)

exhibited few spots of corrosion but after 2400 h almost 1% of the panel surface rusted.

As a general rule, solvent-borne paints did not blister in the humidity chamber, except the paint pigmented with zinc phosphate which had very small blisters with medium surface density after 860 h of essay. All water-borne paints presented small blisters after the exposure to the humidity chamber. The surface density of blisters is lower for the phosphates and increased slightly for the tripolyphosphate due, probably to its high solubility.

The corrosion potential of coated steel and the ionic resistance of the different coatings were employed as a criterion of coating integrity [50–52]. Full protection of the steel substrate was achieved when the corrosion potential was higher than −0.100 V. The corrosion potential of steel coated with the solvent borne paint pigmented with zinc phosphate (paint 1A) dropped after twelve days of testing to ∼−0.600 V (Fig. 10). After a fortnight of immersion, the potential shifted to more positive values due to a re-passivation process to finally decay again, beyond 20 days of immersion. On the other hand, the water-borne paint formulated with zinc phosphate (paint 1B), acquired a corrosion potential which oscillated around −0.250 V during the

immersion period, indicating a much better protection of the steel substrate [50–52].

In the case of paints formulated with zinc molybdenum phosphate (paints 2A and 2B), the corrosion potential of steel oscillated around −0.300 V, thus indicating an acceptable degree of protection of the metal substrate. No significant differences were found between both kinds of paints (Fig. 10).

The most positive corrosion potentials values were observed for paints formulated with zinc tripolyphosphate. The steel coated with the solvent-borne paint (paint 3A) exhibited corrosion potential values which fluctuated around −0.150 V while those of the water-borne coating (paint 3B) were slightly more positive (∼−0.100 V). In both cases, full protection of the metal substrate was accomplished (Fig. 10).

From the preceding discussion, it may be seen that the anti-corrosive behaviour of the pigments was in accordance with their respective corrosion rates. The corrosion potential of steel panels coated with water borne paints is, as a general rule, more positive than that of solvent borne paints due to the beneficial effect of the resin, which reduced steel corrosion rate. This effect was more noticeable for zinc phosphate in the sense that the corrosion potential is much more positive for the water borne coatings than for the solvent one. In the case of zinc molybdenum phosphate, the corrosion potential of both paints oscillated around the same value, approximately −0.300 V, and the action of the resin was less appreciated; the anti-corrosive behaviour seemed to be determined by the intrinsic characteristics of the pigment more than the nature of the binder [53]. These results proved that a careful selection of the resin may lead to efficient water-borne anticorrosive coatings with equal or even better performance than solvent-borne paints.

After one day of immersion, almost all paints showed ionic resistance values higher than $10^6 \ \Omega \ cm^2$, pointing out the existence of an acceptable barrier effect [50–52]. Solvent borne paints pigmented with orthophosphates developed important barrier properties ($R_i > 10^8 \ \Omega \ cm^2$) and maintained high values during, at least, 20 days. The solvent-borne coating formulated with zinc tripolyphosphate lacked this barrier properties but, however, it protected steel due to the combined action of the pigment and the resin
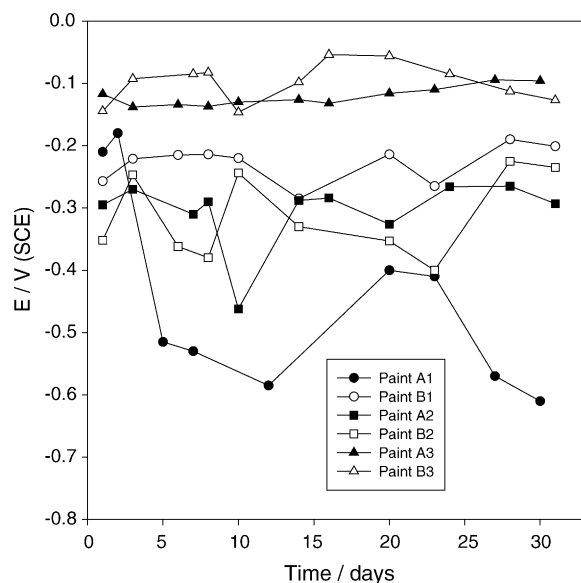

Fig. 10. Corrosion potential of painted steel, as a function of time, in 0.5 M sodium perchlorate.
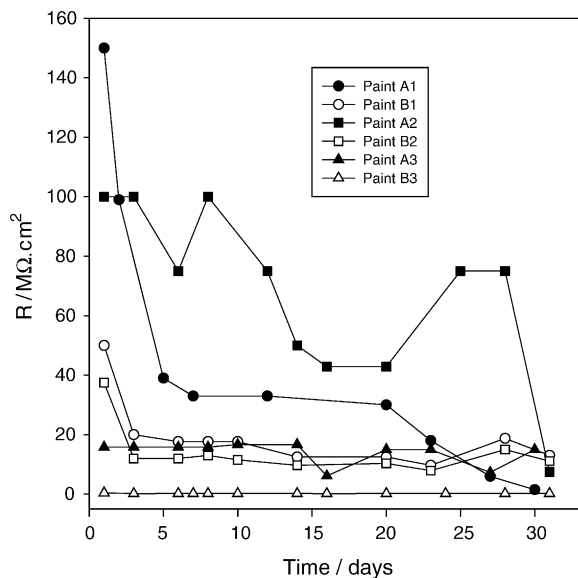
Fig. 11. Ionic resistance of painted steel as a function of time in 0.5 M sodium perchlorate.

(Fig. 11). It must be pointed out that solvent-borne paints developed, as an average, higher ionic resistance values than water-borne coatings. As time elapsed, the ionic resistance of most paints decreased and fluctuated around 12 MΩ, so barrier properties were still important after almost one month of immersion. The lowest ionic resistance was observed for the water-borne paint containing zinc tripolyphosphate which was close to 1 MΩ during the whole testing period but it showed excellent anti-corrosive performance due to the inhibitive pigment and the synergism with the resin. There was observed a residual barrier effect, in all cases, after 1 month of exposure (Ri ≈ 10^6 Ω cm^2).

4. Final considerations

The three types of phosphates tested in this research are able to protect steel when incorporated into a paint formulation. Second generation phosphates may contain chemical species which are able to improve steel protection. In this way, zinc oxide restrains steel corrosion by increasing the pH of the electrolyte solution and polarising cathodic areas. Molybdenum compounds tend to deposit onto the metal surface, thus inhibiting substrate pitting; although no molybdenum was found in the passive layer. Tripolyphosphates, the third generation of phosphate pigments, are characterised by leaching higher amounts of passivating species into solution.

Steel corrosion potential, in every pigment suspension, was more positive than the corrosion potential of steel in the supporting electrolyte; values measured after 24 h of exposure confirmed that corrosion products were a certain type of iron oxyhydroxide layer. In many cases, corrosion products plug the pores opened in the oxide layer. The presence of phosphate anions and other inhibitive species does modify the oxide layer avoiding the growth of expansive oxides; obviously protective films formed on steel strongly depended on the type of pigment.

Steel corrosion rate also diminished in the presence of the different phosphates being zinc molybdenum phosphate and zinc tripolyphosphate the best inhibitors. Polarisation tests also revealed the inhibitive action of the pigments. Lowest critical current density to achieve passivation and lowest current density in the passive zone were observed in the presence of different phosphates. Cathodic curves showed that oxide formation is inhibited and the oxygen reduction current reduced by phosphates.

The anti-corrosive protection of different phosphates studied in this research may be highly influenced by the water-borne resin. Interesting synergism may be achieved between the water-borne resin and the pigments. The resin by itself may reduce steel corrosion rate by depositing onto its surface. The i–E anodic profiles were substantially modified when the epoxy resin was added to the pigment suspension; as a general rule it can be said that the electrochemical reaction is much more polarised and the oxidation peaks appeared at more positive potentials. Electrochemical techniques proved to be useful to detect and study possible synergism among pigments and the water-soluble resin. The best anti-corrosive behaviour in the salt spray test was achieved by water-borne paints as a consequence of the interaction between the resin and the substrate and the resin and the pigments.

Electrochemical tests performed on painted panels showed that zinc molybdenum phosphate and zinc tripolyphosphate had the best anticorrosive behaviour which was in accordance with their respective corrosion rates. The beneficial effect of the water-

soluble resin is more noticeable with the pigment which exhibited the highest corrosion rate. Solvent-borne paints developed, as an average, higher ionic resistance values than water-borne coatings. When the ionic resistance resulted in a low value, indicating the lack of a barrier between the metal and the electrolyte, the anticorrosive protection was supplied by the pigment and, in water borne paints, by the combined action of the pigment and the resin.

Acknowledgements

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