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Zinc hypophosphite: a suitable additive for anticorrosive paints to promote pigments synergism

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Abstract In this investigation, the synergism promoted by zinc hypophosphite in an anticorrosive pigment mixture is reported. This paper describes the anticorrosive behavior of a commercial pigment mixture containing zinc hypophosphite, reduced levels of zinc phosphate, and zinc oxide. The anticorrosive performance of the pigment mixture was assessed by electrochemical techniques (corrosion potential and linear polarization measurements) employing pigment suspensions. The behavior of each separate component of the mixture was also studied in the same way. The nature of the protective layer was investigated by scanning electron microscopy (SEM). In a second stage, the anticorrosive properties of the pigment were assessed by incorporating it into alkyd and epoxy paints that were evaluated by accelerated (salt spray and humidity tests) and electrochemical measurements. Experimental results showed that improved anticorrosion protection is achieved in paints with reduced zinc phosphate contents as a consequence of the synergistic interaction between zinc hypophosphite and the other components of the pigment mixture.

Keywords Anticorrosive paints, Electrochemical tests, Phosphate pigments, Zinc hypophosphite

Introduction

Green chemistry is the discipline that deals with pollution prevention at the molecular level. The efforts in this field are focused on reducing emissions and waste with zero emissions as the goal, developing safer products and processes, conducting life-cycle assessments of the processes, and increasing efficiency in the use of materials, energy, water, etc.[1] In this sense, two major goals from the 1970s were achieved in the field of paint technology: the replacement of toxic inhibitive pigments containing lead and chromate compounds, and the progressive elimination of solvents in paint formulations to fit VOCs regulations.

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, with zinc phosphate being the precursor.[2–26] As a general rule, it can be stated that the protective action of phosphates is due to the formation of an iron oxyhydroxide film on the steel substrate, which is nonexpansive in nature. The polarization of cathodic areas by the precipitation of sparingly soluble salts, which strongly adheres to the surface, also contributes to metal passivation.[3,27,28]

Nontoxic corrosion inhibitors can work synergistically with each other to give a performance greater than either one alone. Lead silicochromate constitutes an early example of synergism and, more recently, the combination of phosphates and borates, organic inhibitors, and phosphates, etc. was reported.[29]

Waterborne coatings are finding more and more importance for both do-it-yourself and industrial coating applications due to the imposition of legislative restrictions on the emission of organic materials to the atmosphere.[30–34] However, waterborne paints are said to be less resistant to the corrosion process and prone to biological attack.[31,35–38] They also exhibit “flash rusting,” which finally affects the appearance of the coating.[35,38,39]

The objective of this research was to study the synergism between a first generation phosphate

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pigment—a ''complementary'' pigment (zinc oxide)—and zinc hypophosphite in a pigment mixture that is commercially available. Zinc hypophosphite could be used as a suitable additive for paints to promote the above-mentioned synergism, which could result in an improved anticorrosive performance. The anticorrosive behavior of the commercial blend was evaluated by electrochemical tests. Then, different coatings were formulated employing the anticorrosive pigment mixture. The behavior of the resulting paints was evaluated through accelerated and electrochemical tests (corrosion potential and ionic resistance).

Experimental

The inhibitive properties of a commercial blend containing zinc phosphate, zinc hypophosphite, and zinc oxide were evaluated by means of electrochemical test in pigment suspensions. This pigment mixture was also used as the inhibitive pigment in paints whose anticorrosive properties were assessed by accelerated and electrochemical tests. The composition of the commercial anticorrosive pigment mixture was determined by conventional analytical procedures. The presence of hypophosphite was confirmed by fourier transform infrared spectroscopy (FTIR) measurements. The solubility of the inhibitive mix was also determined by analytical techniques.

Evaluation of the inhibitive properties of the pigment suspension

The corrosion potential of an SAE 1010 steel electrode was monitored, as a function of time, in the corresponding pigment suspension (pigment mixture or zinc phosphate) in 0.025 M sodium perchlorate, employing a saturated calomel electrode (SCE) as reference.

The morphology of the protective layer formed on the steel panel exposed to the anticorrosive pigment suspension was observed by scanning electron microscopy (SEM) employing a PHILLIPS SEM 505 coupled with an EDAX OX PRIME 10 (energy-dispersed form) to determine the surface composition that was expressed as percentage of the elements that constitute the different compounds.

Anodic and cathodic polarization curves of a SAE 1010 steel electrode with low surface roughness (mean peak-to-valley height of 1.40 μm), were obtained after 4 h of exposure to the pigment mixture suspension in 0.5 M sodium perchlorate solution. Sodium perchlorate solution was chosen as a supporting electrolyte to avoid the intense corrosion produced by sodium chloride, which could make it impossible to observe the different processes that take place on the electrode. A SCE was used as a reference and a platinum grid was used as the counter electrode. The sweep began in the vicinity of the corrosion potential at a scan rate of 1 mVs^{-1}. Similar curves were obtained for each component of the blend to determine its influence on the anticorrosive behavior of the pigment mixture. Steel corrosion rate was determined from polarization measurements. Measurements were carried out with a Potentiostat-Galvanostat EG&G PAR Model 273A plus SOFTCORR 352 software.

Paint composition, preparation, and application

Three kinds of paints were formulated—two of them of the epoxy type (a waterborne paint and a solventborne paint), and the other an alkyd solventborne paint. The composition of all paints can be seen in Table 1.

An epoxy resin, based on a mix of bisphenol A and bisphenol F, was selected to formulate the waterborne paint. The curing agent (hardener), which also acts as an emulsifier, was a modified polyamidoamine that was

Table 1: Composition of paints as volume %

Components	Paints					
	1	2	3	4	5	6
Anticorrosive pigment mixture	1.8	3.6	3.0	6.0	3.0	6.0
Titanium dioxide	2.6	2.1	2.6	2.4	2.6	2.4
Talc	2.5	2.1	7.2	5.8	7.2	5.8
Barite	2.8	2.2	7.2	5.8	7.2	5.8
Mica	2.3	2.0	–	–	–	–
Waterborne epoxy resin (1:1)	47.7	47.7	–	–	–	–
Epoxy resin (1:1)	–	–	55.8	55.8		
Alkyd resin (1:1)	–	–	–	–	55.8	55.8
Water	38.9	38.9	–	–	–	–
Xylene/methylisobuthylketone/buthyl cellosolve (13%/45%/42% by weight)	–	–	24.2	24.2	–	–
White spirit	–	–	–	–	24.2	24.2
Additives	1.4	1.4	–	–	–	–

50% solid. The resin/hardener ratio was 1.0/1.2 parts by weight. Neutral demineralized water was employed as a solvent. The anticorrosive pigment content was 15% and 30% by volume with respect of the total pigment content, and titanium dioxide, barium sulfate, talc, and mica were incorporated to complete the pigment formula. Mica was added due to its barrier properties and the ability to reduce ''flash rusting.'' Pigment volume concentration (PVC) was 20% to produce a more impervious coating. Waterborne paint manufacturing was carried out employing a high-speed disperser. Preliminary tests showed the advantage of incorporating the pigment into the hardener instead of mixing it with the resin. Water was added first because of the relatively high viscosity of the hardener, and then the pigments were incorporated in accordance with their increasing oil absorption index. Mica was added at the end of the process to avoid the break-up of laminar particles.

It was decided that the anticorrosive properties of the pigment employing solventborne paints should be checked because their behavior has been well-documented for many years. The resin employed to formulate the solventborne epoxy paint was a bisphenol epoxy-polyamide resin (1:1 ratio v/v). The solvent was a mixture of xylene/methyl isobutyl ketone/butyl cellosolve (13/45/42%, by weight). The PVC/critical PVC (CPVC) ratio was 0.8 as suggested elsewhere.[10,11] The anticorrosive pigment load was 15% and 30% v/v of the total pigment content—the same pigment content suggested when orthophosphates are employed as anticorrosive pigments. Titanium dioxide, barium sulfate, and talc were incorporated to complete the pigment formula. All pigments were dispersed for 24 h in the vehicle employing a ball mill, to achieve an acceptable dispersion degree.

The resin used to make the solventborne alkyd paint was a medium oil alkyd (50% linseed oil, 30% o-phtalic anhydride, 8% pentaerythritol and glycerol, and 12% pentaerythritol resinate); the solvent was white spirit. The anticorrosive pigment content was also 30% by volume, as suggested in the literature for phosphate pigments.[10,11] The PVC/CPVC relationship was also 0.8. The procedure to prepare the alkyd paint was the same one depicted before for the solventborne epoxy coatings.

SAE 1010 steel panels (15.0 × 7.5 × 0.2 cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene, and then painted by brushing—up to a thickness of 75 ± 5 μm. Painted panels were kept indoors for 7 days before being tested.

The performance of anticorrosive paints through accelerated and electrochemical tests

A set of three panels was put in the salt spray chamber (ASTM B 117) to evaluate the degree of rusting (ASTM D 610) and blistering (ASTM D 714). Painted panels were evaluated after 1000, 1700, and 1950 h of exposure; the mean value of the obtained results was reported in this paper. A similar set was placed in the humidity chamber (ASTM D 2247); and the degree of blistering and rusting was evaluated after 400, 1900, and 2400 h.

The electrochemical cells employed to evaluate the anticorrosive 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 0.5 M sodium perchlorate. 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. The corrosion potential (E_{corr}) of coated steel was measured employing an SCE as reference and a high impedance voltmeter.

Results and discussion

The composition of the commercial pigment mixture tested in this research was as follows: 41.6% zinc phosphate ($Zn_3(PO4)_2 \cdot 4H_2O$), 10.8% zinc hypophosphite ($Zn(PO_2H_2)_2 \cdot H_2O$), and 47.6% zinc oxide (ZnO). The presence of hypophosphite anion was confirmed by the absorption band at 1700 cm^{-1} in the FTIR spectrum, which corresponds to the stretching of the P–H bond. The concentration of the inhibitive species in the pigment-saturated solution (phosphate anion and zinc cation,[2]) was obtained according to ASTM D 2448. The phosphate concentration was found to be equal to 13 ppm, and it was higher than the value reported for zinc phosphate alone (1 ppm). The zinc content was 15 ppm—an intermediate value between that of hydrated zinc phosphate (5 ppm) and hydrated organic modified zinc phosphate (80 ppm).[10,11]

Evaluation of the inhibitive properties of the pigment suspension

The pigment mixture containing zinc hypophosphite slightly displaced the corrosion potential towards more positive values, with respect to zinc phosphate alone, at the beginning of the test period (Fig. 1). The protective layer formed on steel in contact with the pigment mixture suspension was a uniform one, and was mainly constituted by iron compounds (Fe: 85.6%) and a rather high zinc content, 14.4% (Fig. 2a). Because nonmetallic elements were not detected on the scanned surface, it was concluded that primarily oxyhydroxides were formed. In an interesting experiment, Pourbaix demonstrated that cavities on a corroding surface are anodic in depth and cathodic near the surface.[40] This was why globular formations observed in Fig. 2b contained high amounts of Zn (58.3%), with Fe constituting the rest. It is thought that the composition of the protective layer surrounding the

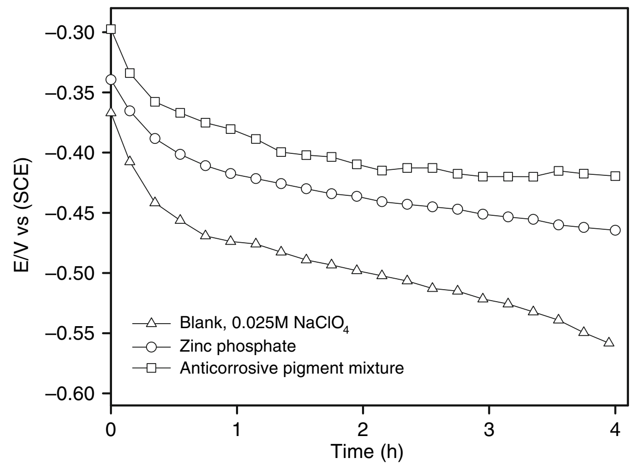

Fig. 1: Corrosion potential of SAE 1010 steel in pigment suspensions. Electrolyte: 0.025 M $NaClO_4$

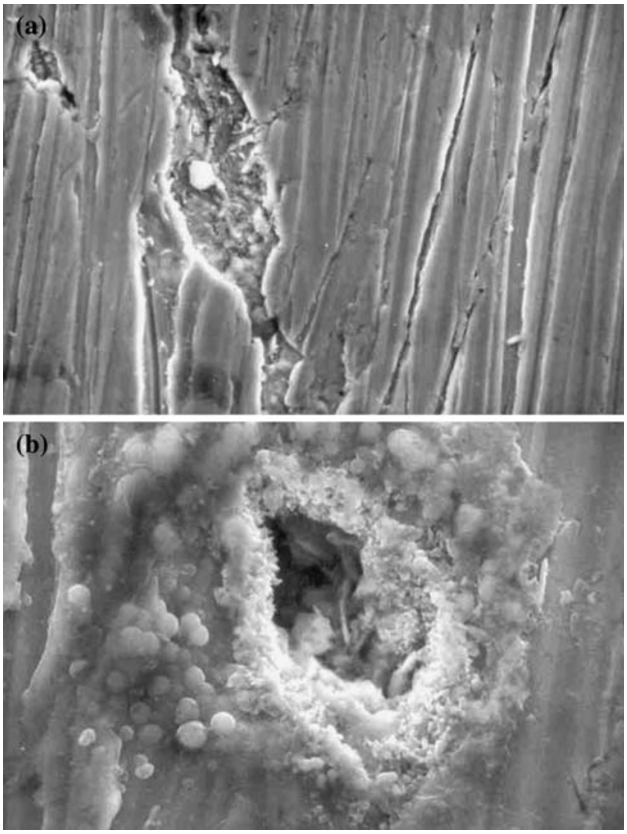

Fig. 2: SEM micrograph of the SAE 1010 steel surface after 24 h contact with the anticorrosive pigment suspension in 0.025 M $NaClO_4$. (a) Panoramic view (1500×); (b) oxide formations surrounding a cavity (2500×)

cavity was enriched with zinc compounds that precipitated as a result of the alkalinization of cathodic areas.

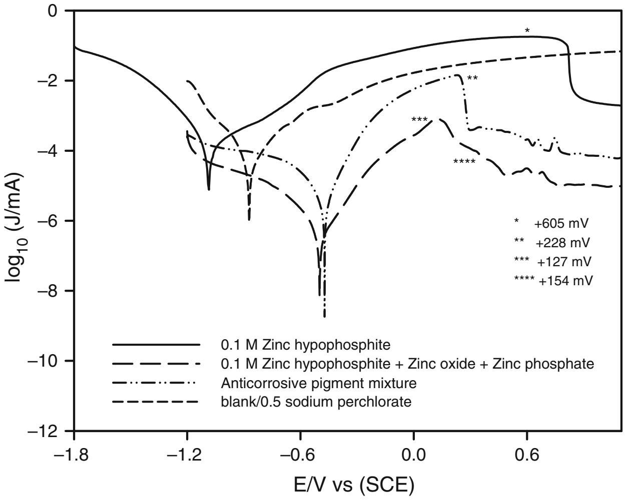

Fig. 3: Tafel polarization curves of the SAE 1010 steel electrode in the pigments suspensions after 6 h of exposure. Electrolyte: 0.5 M $NaClO_4$. Scan rate 3 mV s^{-1}

Figure 3 depicts polarization curves for different suspensions containing zinc hypophosphite. One of these systems was similar to the commercially available anticorrosive blend. Results are compared with a blank containing the supporting electrolyte. The anodic branch of the polarization curve of the supporting electrolyte increased continuously as the electrode potential increased and the cathodic current was found to be 188 $\mu A.cm^{-2}$. The presence of zinc hypophosphite caused the electrode to passivate during the anodic scan, exhibiting a peak at +605 mV (peak current 179 $mA.cm^{-2}$). The cathodic current was high and similar to that measured with the blank. The addition of zinc oxide and zinc phosphate to the solution also caused the electrode to passivate. Two overlapped peaks at +127 mV (peak current 2.99 $mA.cm^{-2}$) and at +154 mV (peak current 2.41 $mA.cm^{-2}$), respectively, appeared in the voltammogram. The presence of zinc oxide and zinc phosphate modified the passivity achieved with zinc hypophosphite in the sense that it appeared at lower potentials and with much lower peak currents. The presence of these substances also diminished the cathodic current to 2.53 $\mu A.cm^{-2}$. It was thought that zinc hypophosphite accelerated steel dissolution but the presence of zinc oxide and zinc phosphate, together with the products of steel dissolution, yielded the growth of an effective passive layer. This synergism is beneficial for steel passivation because not only was anodic passivation improved but cathodic current also diminished markedly. Results obtained with the commercial blend were similar; an anodic passivation peak was observed at +228 mV (peak current 47.7 $mA.cm^{-2}$) and the oxygen current was also low (11 $\mu A.cm^{-2}$).

The performance of anticorrosive paints in accelerated tests

Results obtained in the salt spray test after 1950 h showed that the best anticorrosive behavior was

Table 2: *Rusting (ASTM D 610) and †blistering (ASTM D 714) degrees of painted panels exposed to the salt spray chamber (ASTM B 117)

Paints	Time/Hours					
	1000		1700		1950	
	R*	B†	R*	B†	R*	B†
1	9	10	8	8 M	8	8MD
2	9	10	9	10	9	10
3	10	10	8	8F	6	8F
4	10	10	9	4F	7	2F
5	10	8F	9	6F	9	6F
6	9	10	9	6F	9	6F

*R: Rusting degree (ASTM D 610)

Rust grade	10	9	8	7	6	5	4	3	2	1
Rusted area/%	No rusted	0.03	0.1	0.3	1	3	10	16	33	50

†B: Blistering degree (ASTM D 714)

Frequency	Dense, D	Medium dense, MD	Medium, M	Few, F
Size	10	8	6, 4	2
Comments	No blistering	Smaller size blister easily seen by unaided eye	Progressively larger sizes	

achieved by waterborne epoxy (paints 1 and 2) and alkyd (paints 5 and 6) coatings. The performance of solventborne epoxy coatings was less satisfactory (Table 2). The waterborne epoxy paint exhibited a striking behavior—obtaining a qualification 7 after 3700 h of testing. It was reported that similar paints formulated only with 30% zinc phosphate behaved satisfactorily during 2400 h of exposure in the salt spray chamber.[41] Solventborne epoxy paints began to fail, after an average of 1950 h of exposure, while similar paints with 30% zinc phosphate achieved an acceptable degree (qualification 7) for up to 1700 h of exposure.[27,41] The results obtained with the alkyd coating containing the pigment mixture tested in this research were clearly superior to those obtained with zinc phosphate alone. The former paint underwent 1950 h of testing with a qualification equal to 9, while paints formulated with 30% zinc phosphate begun to fail at 1700 h, as was reported in the literature.[27] This improved behavior could be attributed to the reaction of zinc oxide with oleoresinous binders, such as alkyds, to generate zinc soaps that are thought to inhibit corrosion.[42]

The employment of the tested anticorrosive pigment mixture led to very good results even with the lowest pigment content (15%); indeed, no significant differences were observed between both pigment loads employed in this research. Blistering appeared, in most cases, after 1700 h of exposure except for paint 2, which attained a qualification equal to 10 (absence of blistering) during the whole test period.

It was theorized that the pigment mixture restrained the formation of corrosive products, which can disrupt through the paint film. In fact, after paint removal of panels exposed to the salt spray chamber, it was noticed that thick black iron oxide films developed under blisters and a nonexpansive oxide layer grew in the remainder of the surface. A similar dark oxide was reported previously by Amin et al.,[43] who attributed an exceptional corrosion resistance to this layer constituted by a divalent cation, a trivalent one, and anion-like chloride. So, it was speculated that the main function of zinc hypophosphite was to prevent the oxidation of ferrous species into ferric ones to yield the formation of this dark oxide.

The foregoing results pointed out that it is possible to reduce the zinc phosphate content in the paint film if a suitable additive, such as zinc hypophosphite, is incorporated into the formulation to enhance its protective ability. The two anticorrosive pigment loadings employed in this research (15% and 30% v/v, respectively) contained 7.3% and 14.6% zinc phosphate. This calculation was made on the basis of the pigment composition given in the first paragraph of this section and the zinc phosphate density (3.0 g cm^{-3}). These very low zinc phosphate contents could not provide a satisfactory anticorrosive behavior, as reported in previous work.[10,11,27,44] In previous research, it was demonstrated that zinc oxide could improve the inhibitive action of zinc phosphate.[45] In brief, the good anticorrosive performance of tested paints could be attributed to the synergism of the three compounds included in the anticorrosive mixture.

Results in the humidity chamber showed that only waterborne coatings blistered (Table 3). Blistering was observed after 400 h of exposure in the case of the coating with 15% of the anticorrosive blend, and after

Table 3: Rusting (ASTM D 610) and blistering (ASTM D 714) degrees of painted panels exposed to the humidity chamber (ASTM D 2247)

Paints	Time/Hours					
	400		1900		2400	
	R*	B†	R*	B†	R*	B†
1	6	6MD	–	–	–	–
2	10	10	10	8MD	10	8MD
3	10	10	10	10	10	10
4	10	10	10	10	10	10
5	10	10	10	10	10	10
6	10	10	10	10	10	10

*,†See Table 2 footnote

1900 h with the other paints. In the latter case, the blistering remained constant (degree 8MD) during the rest of the test period. None of the paints showed signs of corrosion during the exposure time.

The performance of anticorrosive paints in electrochemical tests

Solventborne paints showed very good barrier properties at the beginning of the immersion period. The highest ionic resistance was measured for alkyd paints. Ionic resistance began to decrease after the first day of immersion, and it decreased faster for epoxy coatings during the first 14 d of immersion. The unusual behavior of alkyds was attributed to the interaction of the binder with zinc oxide, which may result in a more impervious film.[42–47] As it occurred in other cases, waterborne paints did not exhibit a significant barrier effect; ionic resistance was too low from the very beginning of the test period (Fig. 4).

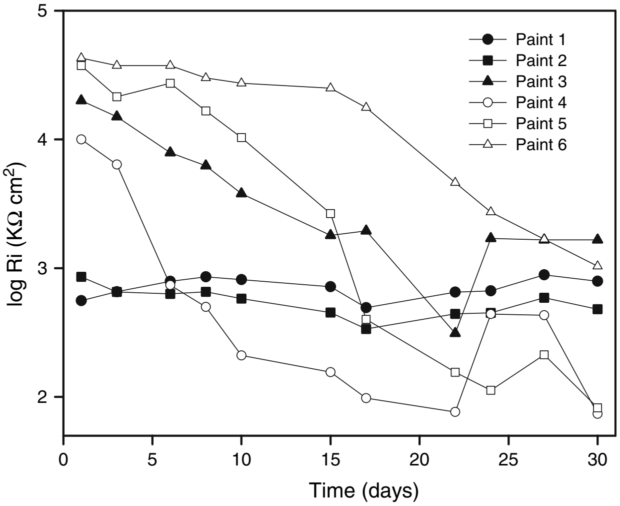

Fig. 4: Ionic resistance of painted steel, as a function of time, in 0.5 M sodium perchlorate

As a general rule, it may be said that corrosion potential varied jointly with the ionic resistance as time elapsed. The E_{corr} of panels coated with the epoxy waterborne paints fluctuated around ~ -0.340 V from the first 14 d of immersion until the end of the test; this is to say that they maintained far from typical values of corroding steel. Because the ionic resistance of these paints is rather low, it was believed that some inhibitive species was formed as a consequence of pigment-binder interaction. In the case of solventborne epoxies, E_{corr} maintained higher (~ -0.200 V) for the lower pigment content and decreased significantly, (-0.525 V) at the end of the test. As the ionic resistance is lower than the expected values for an epoxy coating,[2,7,12,13] it was considered that there was some kind of incompatibility between the pigment and the epoxy resin. However, solventborne epoxies showed a certain tendency to repassivation after 3 weeks of immersion. Alkyds showed an improved anticorrosive performance because their E_{corr} was higher than -0.200 V during the first week of immersion and was more positive for the highest pigment content.[2,7,12,13] As was said previously, this behavior was due to the interaction of the binder with zinc oxide[42–47] (Fig. 5).

Conclusions

Accelerated tests showed that the pigment mixture is suitable for formulating waterborne epoxy coatings and alkyd paints that show an improved anticorrosive behavior. The main function of zinc hypophosphite seems to be to accelerate steel dissolution to form a better protective layer. Zinc compounds can also help polarize cathodic sites. Good results were obtained with the lowest pigment content. This fact implies that the phosphate content can be reduced significantly when employing zinc hypophosphite and zinc oxide in combination with zinc phosphate.

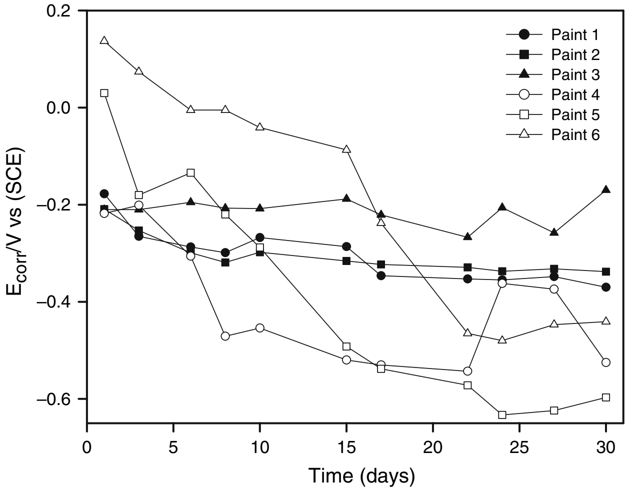

Fig. 5: Corrosion potential of painted steel, as a function of time, in 0.5 M sodium perchlorate

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References

1. Darling, D, Rakshpal, R, "Green Chemistry Applied to Corrosion and Scale Inhibitors." *Mater. Perform.*, **37** (12) 42–45 (1998)
2. Romagnoli, R, Vetere, VF, "Heterogeneous Reaction Between Steel and Zinc Phosphate." *Corrosion (NACE)*, **51** (12) 116–123 (1995)
3. Szklarska-Smialowska, Z, Mankowsky, J, "Cathodic Inhibition of the Corrosion of Mild Steel in Phosphate, Tungstate, Arsenate and Silicate Solutions Containing Ca^{2+} ions." *Brit. Corros. J.*, **4** (9) 271 (1969)
4. Meyer, G, "Uber Zinkphosphat und Bariumchromat als moderne Korrosionsinhibitoren." *Farbe Lack*, **69** (7) 528–532 (1963)
5. Barraclouugh, J, Harrison, JB, "New Leadless Anti-Corrosive Primers." *JOCCA*, **48** (4) 341–355 (1965)
6. Fragata, FL, Dopico, JE, "Anticorrosive Behaviour of Zinc Phosphate in Alkyd and Epoxy Binders." *JOCCA*, **74** (3) 92–97 (1991)
7. Romagnoli, R, Vetere, VF, "Non Pollutant Corrosion Inhibitive Pigments: Zinc Phosphate, a Review." *Corros. Rev.*, **13** (81) 45–64 (1995)
8. Svoboda, M, Mleziva, J, "Properties of Coatings Determined by Anticorrosive Pigments." *Prog. Org. Coat.*, **12** 251–297 (1984). doi:10.1016/0033-0655(84)80011-4
9. Chromy, L, Kaminska, E, "Non-Toxic Anticorrosive Pigments." *Prog. Org. Coat.*, **18** 319–324 (1990). doi:10.1016/0033-0655(90)85014-O
10. Gerhard, A, Bittner, A, "Second Generation Phosphate Anti-Corrosive Pigments. Formulating Rules for Full Replacement of New Anti-Corrosive Pigments." *J. Coat. Technol.*, **58** (740) 59–65 (1986)
11. Bittner, A, "Advanced Phosphate Anticorrosive Pigments for Compliant Primers." *J. Coat. Technol.*, **61** (777) 14–118 (1989)
12. Romagnoli, R, del Amo, B, Vetere, VF, Vèleva, L, "High Performance Anticorrosive Epoxy Paints Pigmented with Zinc Molybdenum Phosphate." *Surf. Coat. Int.,*, **83** (1) 27–32 (2000). doi:10.1007/BF02692684
13. del Amo, B, Romagnoli, R, Vetere, VF, "Study of the Anticorrosive Properties of Zinc Phospahte and Zinc Molybdophosphate in Alkyd Paints." *Corros. Rev.*, **14** (1–2) 121 (1996)
14. Vetere, VF, Romagnoli, R, "Role of Calcium Acid Phosphate as Corrosion Inhibitive Pigment." *Brit. Corros. J.*, **29** (2) 115 (1994)
15. Del Amo, B, Romagnoli, R, Vetere, VF, "Steel Corrosion Protection by Means of Alkyd Paints Pigmented with Calcium Acid Phosphate." *Ind. Eng. Chem. Res.*, **38** 2310–2314 (1999). doi:10.1021/ie9805638
16. Taketani, Y, Kondo, H, Kropman, M, "Propietary Aluminium Triphosphate Pigments for Waterborne Coatings." *Polym. Paint Col. J.*, **183** (4329) 270–271 (1993)
17. Jackson, KG, Kropman, M, "Novel Waterborne High Performance Steel Primers." *Polym. Paint Col. J.*, **178** (4129) 559–561 (1988)
18. Takahashi, M, "Characteristics and Applications of Aluminium Triphosphate as Special Chemical." *Polym. Paint Col. J.*, **174** (4133) 281–284 (1984)
19. Kamiya, K, Okuda, M, Okajima, M, "Combination Effect of K-White and Chromate Pigments in Coil Coatings Systems." *Polym. Paint Col. J.*, **178** (4228) 974–980 (1988)
20. Nakano, J, Murakami, M, Okuda, M, "Aluminium Triphosphate-Salt Spray Studies." *Polym. Paint Col. J.*, **177** (4199) 642–645 (1987)
21. Nishihara, M, Nakano, G, Kobayashi, M, Nagita, M, Murakami, M, "Studies on Anticorrosive Properties of Aluminium Triphosphate Pigments. Corrosion Inhibition Properties in Alkyd Resin Coatings System." *Polym. Paint Col. J.*, **174** (4125) 590–597 (1984)
22. Noguchi, T, Nahono, J, Kabayashi, M, Nagita, M, Kinugasa, M, Murakami, M, "Studies on Anticorrosive Properties of Aluminium Triphosphate Pigments. Corrosion Inhibition Properties in Epoxy Resin Coatings System." *Polym. Paint Col. J.*, **174** (4133) 888–891 (1984)
23. Deyá, M, Vetere, V, Romagnoli, R, del Amo, B, "Aluminium Tripolyphosphate Pigments for Anticorrosive Paints." *Pig. Res. Technol.*, **30** (1) 13–24 (2001). doi:10.1108/03699420110364129
24. Vetere, V, Deyá, M, Romagnoli, R, del Amo, B, "Calcium Tripolyphosphate: An Anticorrosive Pigment for Paints." *J. Coat. Technol.*, **73** (917) 57–63 (2001). doi:10.1007/BF02698398
25. Deyá, M, Blustein, G, Romagnoli, R, del Amo, B, "The Influence of the Anion Type on the Anticorrosive Behaviour of Inorganic Phosphates." *Surf. Coat. Technol.*, **150** 133–142 (2002). doi:10.1016/S0257-8972(01)01522-5
26. Deyá, M, Vetere, VF, Romagnoli, R, Del Amo, B, "Zinc Tripolyphosphate: An Anticorrosive Pigment for Paints." *Surf. Coat. Int.*, **86** (B1) 79–85 (2003)
27. Blustein, G, del Amo, B, Romagnoli, R, "The Influence of the Solubility of Zinc Phosphate Pigments on Their Anticorrosive Behaviour." *Pig. & Res. Technol.*, **29** (2) 100–107 (2000). doi:10.1108/03699420010319148
28. Prior, MJ, Cohen, M, "The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors." *J. Electrochem. Soc.*, **100** (5) 203–215 (1953). doi:10.1149/1.2781106
29. Hodges, SA, Uphues, WM, Tran, MT, "Non-Toxic Corrosion Inhibitive Synergistic System." *Surf. Coat. Int.*, **4** 178 (1997). doi:10.1007/BF02692639
30. Nicholson, JW, "Waterborne Coatings: A Review of Basic Principles." *JOCCA*, **70** (1) 1–4 (1987)
31. Swaraj, P, (ed.), "Waterborne Coatings" in Surface Coatings. *Science and Technology*, 2nd ed., J. Wiley & Sons, Great Britain (1997)
32. Masciale, MJ, "Water-Bornes and High Solids: Innovative Applications." *Eur. Coat. J.*, **1–2** 16–27 (1995)
33. van der Kolk, CEM, Kruijt, R, de Rouville, EA, "Water-Based Acrylic Dispersion Paints for the Protection of Structural Steel; A Technology in Full Development." *JOCCA*, **76** (7) 280–286 (1993)
34. Padget, JC, "Polymers for Water-Based Coatings—A Systematic Overview." *J. Coat. Technol.*, **66** (839) 89–105 (1994)
35. Reinhard, G, "Formulation of Water-Borne Dispersions for Corrosion-Protective Primers." *Prog. Org. Coat.*, **18** 123–145 (1990). doi:10.1016/0033-0655(90)85008-L
36. Spengler, E, Fragata, FL, Margarit, ICP, Mattos, OR, "Corrosion Protection of Low Toxicity Paints." *Prog. Org. Coat.*, **30** 51–57 (1997). doi:10.1016/S0300-9440(96)00668-6

37. Reinhardt, G, Rammelt, U, Moll, A, "Zur Pigmente von Wasserlacken fur den Korrosionsschutz." *Farbe Lack*, **102** (5) 58–67 (1996)
38. Jackson, K, "Recent Advances in Water-Borne Protective Coatings." *Surf. Coat. Int.*, **82** 340–343 (1999). doi:10.1007/BF02720130
39. Gee, S, "Water Borne Coatings." *Surf. Coat. J.*, **80** (7) 316–322 (1997). doi:10.1007/BF02692678
40. Pourbaix, M, *Lecciones de Corrosión Electroquímica (original title: "Leçons en Corrosion Electrochimique", CEBELCOR, Belgium)*, p. 264. Instituto Español de Corrosión y Protección, Madrid (1987)
41. Blustein, G, Deyá, MC, Romagnoli, R, del Amo, B, " Three Generations of Inorganic Phosphates in Solvent and Water-Borne Paints: A Synergism Case." *Appl. Surf. Sci.*, **252** 1386 (2005). doi:10.1016/j.apsusc.2005.02.096
42. Kroustein, M, "Zinc Oxide Complexes in Protective Oils on Galvanised Steel." *JOCCA*, **74** (4) 124–132 (1991)
43. Amin, S, Avudaiappan, S, Johnpasha, A, Provder, T, Floyd, FL, "Elucidation of Corrosion Failure Mechanisms of Coated Phosphated Steel Substrates." *J. Coat. Technol. Res.*, **5** (3) 311–325 (2008). doi:10.1007/s11998-008-9088-6
44. del Amo, B, Romagnoli, R, Vetere, VF, Hernández, LS, "Study of the Anticorrosive Properties of Zinc Phosphate in Vinyl Paints." *Prog. Org. Coat.*, **33** 28 (1998). doi:10.1016/S0300-9440(97)00124-0
45. Deyá, MC, Romagnoli, R, del Amo, B, "The Influence of Zinc Oxide on the Anticorrosive Behaviour of Eco-Friendly Paints." *Corros. Rev.*, **22** (1) 1–17 (2004)
46. Johnson, WC, "Cost-Effective Pigmentation in Alkyd Primers for Steel: Barrier Anti-Corrosion Mechanism." *J. Coat. Technol.*, **66** 47–54 (1994)
47. Yang, LH, Lin, FC, Han, EH, "Effects of P/B on the Properties of Anticorrosive Coatings with Different Particle Size." *Prog. Org. Coat.*, **53** 91–98 (2005). doi:10.1016/j.porgcoat.2005.01.003