

Zinc tripolyphosphate: An anticorrosive pigment for paints

M Deyá,¹ V F Vetere,² R Romagnoli^{2,3}
and B del Amo³

1 CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas (CIC-CONICET), Calle 52 e/ 121 y 122 (B1900AYB)
La Plata, Argentina

3 Becario CONICET, 2 Profesor Facultad de Ciencias Exactas, UNLP,
3 Investigador CONICET

Summaries

Zinc tripolyphosphate: An anticorrosive pigment for paints

The aim of this paper was to study the efficiency of zinc tripolyphosphate as an anticorrosive pigment for paints. A procedure to prepare the pigment was outlined and its anticorrosive properties evaluated following the electrochemical behaviour of a steel electrode in pigment suspensions. In a second stage, solvent-borne paints containing barium sulphate, talc and titanium dioxide together with 30 or 10% v/v (by volume) of zinc tripolyphosphate, with respect to the total pigment content, and PVC/CPVC (pigment volume concentration/critical pigment volume concentration) ratio 0.8 were formulated. Two resins were chosen as film-forming materials: an alkyd and an epoxy-polyamide (1:1) resin. The performance of the resulting anticorrosive paints was assessed by accelerated (salt-spray and humidity chambers) and electrochemical tests (corrosion potential, ionic resistance and polarisation resistance).

It was demonstrated that zinc tripolyphosphate inhibited corrosion when incorporated into a paint film. It showed an excellent performance when employed with the alkyd resin. Good correlation was obtained between accelerated and electrochemical tests.

Le Tripolyphosphate de zinc: un pigment anticorrosif pour les peintures

Cet article a comme but l'étude de l'efficacité du tripolyphosphate de zinc en tant que pigment anticorrosif pour la peinture. Les grandes lignes des procédés de préparation ont été exposées et ses propriétés anticorrosives ont été évaluées selon le comportement d'une électrode d'acier dans des suspensions du pigment. Au cours d'une deuxième étape on a formulé des peintures diluables au solvant et contenant du sulfate de baryum, du talc, et du dioxyde de titane aussi bien que 30 ou 10% v/v du pigment tripolyphosphate de zinc par rapport au contenu total en pigments dans le rapport de 0.8 CPV/CPVC (concentration pigmentaire volumique /concentration pigmentaire volumique critique). Deux résines ont été choisies pour former le film, l'une alkyde, l'autre une époxy-polyamide (1:1). La performance des peintures anticorrosives qui en provenaient a été évaluée par des essais accélérés (enceintes d'essais en brouillard salin et en humidité) et par des essais électrochimiques (potentiel de corrosion, résistance ionique, résistance de polarisation).

Nous avons démontré que le tripolyphosphate de zinc quand il est incorporé à un film de peinture inhibe la corrosion. Il a fait preuve d'une performance excellente quand il était employé avec la résine alkyde. Il y avait une bonne corrélation entre les résultats des essais accélérés et ceux des essais électrochimiques.

Zinktripolyphosphat: Ein korrosionshemmendes Farbpigment

Der Zweck dieser Studie war es, die Wirksamkeit von Zinktripolyphosphat als ein korrosionshemmendes Pigment für Anstrichfarben zu untersuchen. Wir stellten zunächst eine Methode vor, um das Pigment herzustellen, und bewerteten dann seine antikorrosiven Eigenschaften mittels der elektrochemischen Reaktion einer Stahl-Elektrode in einer Pigmentsuspension.

In einem zweiten Schritt wurden lösungsmittelhaltige Farben hergestellt, die Bariumsulfat, Talk und Titandioxid, sowie einen Anteil von 10% v/v oder 30% v/v des Zinktripolyphosphat (bezogen auf den Gesamtpigmentgehalt) enthielten. Die Farben hatten ein Verhältnis von Pigmentvolumenkonzentration zu kritischer Pigmentvolumenkonzentration von 0.8. Wir verwendeten zwei verschiedene Harze als Filmbildner in diesen Farben: ein Alkyd und ein Epoxy-Polyamid (1:1) Harz. Die Wirksamkeit des entstandenen korrosionshemmenden Lackes wurde mittels beschleunigten Tests (Salzprüher und Luftfeuchtigkeitsräume) und elektrochemischer Tests (Korrosionspotential, ionischer Widerstand, Polarisationswiderstand) ermittelt.

Die Tests untermauerten, daß Zinktripolyphosphat als Bestandteil einer Farbe oder eines Lackes korrosionshemmend wirkt. Zinktripolyphosphat zeigte eine hervorragende Leistung als Bestandteil eines Lackes auf Alkydbasis. Wir fanden auch eine gute Korrelation zwischen den beschleunigten Tests und den elektrochemischen Tests.

For correspondence contact

M Deyá

CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas (CIC-CONICET), Calle 52 e/ 121 y 122 (B1900AYB)
La Plata, Argentina

Tel: +54 221 483 1142
Fax: +54 221 427 1537

Email: estelectro@cidepint.gov.ar

Copyright OCCA 2003

Introduction

Anti-corrosive protective coatings are a key area in the paint industry which is being influenced by modern legislation, and the advent of new technologies for paint formulation and application. The aim of these new technologies is to diminish environmental risk.

Low environmental impact is achieved by reducing or eliminating organic solvents in paint formulation and incorporating non-toxic pigments, especially in the case of anticorrosive formulations. Classic anticorrosive pigments, such as chromates and lead compounds, are being substituted by eco-friendly compounds such as inorganic phosphates and related compounds.

Among the numerous corrosion-inhibitive substances, typically classified as environmentally-compatible products, those based on phosphate pigments dominate the market. For several decades zinc phosphate has been used as a replacement for chromates and lead oxides. The anticorrosive efficiency of zinc phosphate and the way it protects steel are still under discussion. Good results were obtained when zinc phosphate was employed in long-term tests while accelerated tests seemed to lead to disappointing results.¹⁻³ At least, it was clear that the performance of zinc phosphate was inferior to that of zinc chromate in most primer systems.⁴ However, paints containing zinc phosphate showed good performance in acidic atmospheres and industrial environments.^{5,6} Modified zinc phosphates were obtained from zinc phosphate by modifying it with aluminium phosphate, zinc molybdate, zinc oxide, etc. The better performance of modified zinc phosphates has been clearly established by different authors.^{4,7,8}

Pigments containing the triphosphate anion were introduced into the market in order to match more demanding applications. Among these pigments, aluminium triphosphate was widely used. Aluminium triphosphate was employed with various binders and was particularly effective on cross-cuts of rapidly corroding coatings.⁹⁻¹¹ The great acidity of this pigment made it necessary to employ other pigments capable of neutralising this acidity. The presence of pigments other than aluminium triphosphate may affect the formation of an adequate protective layer.¹²

The objective of this research was to study the performance of zinc triphosphate as an anticorrosive pigment for paints. The pigment was prepared at laboratory scale and its inhibitive properties on steel corrosion were assessed by electrochemical techniques. Finally, the anticorrosive performance of the pigment was also evaluated in paints by accelerated and electrochemical tests.

Experimental

Pigment preparation

Zinc triphosphate was obtained in the laboratory by precipitation from sodium triphosphate and zinc nitrate solutions. The adequate pH to precipitate zinc triphosphate was determined from acid-base titration curves. In this sense, an acid solution of 0.1N sodium triphosphate and 0.1N zinc sulphate was titrated with a 0.1N sodium hydroxide, registering the pH of the solution with a glass electrode. In addition, a similar acid solution of zinc sulphate was titrated with 0.1N sodium hydroxide to know the precipitation pH of zinc hydroxide. The titration curves of both systems can be seen in Figure 1. From these curves, the optimum pH value to precipitate zinc triphosphate and to avoid the precipitation of the hydroxide was found to be equal to 5.1.

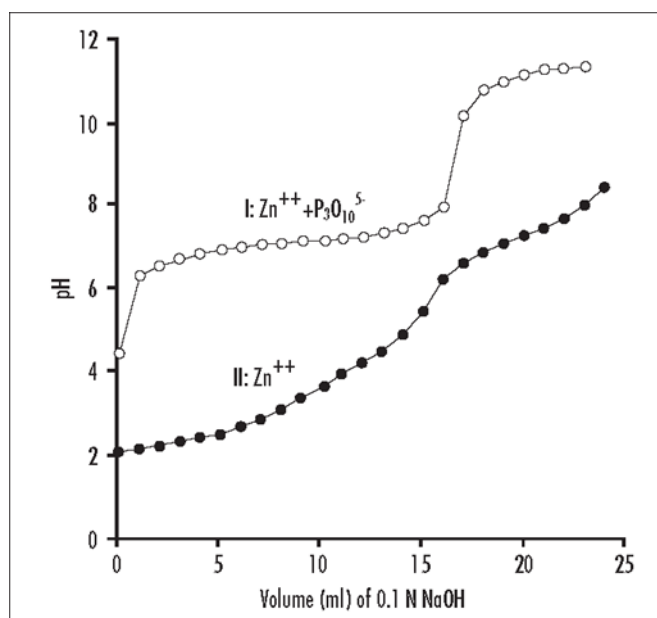


Figure 1: Acid-base titration curve of zinc salts in the presence of sodium triphosphate

Thus, according to the preceding information, zinc triphosphate was obtained by simultaneously dropping 0.1N sodium triphosphate (pH 4) and 0.1N zinc nitrate, at the same pH value, into a glass container. Afterwards, the pH was adjusted at 5.1 by adding a 20% sodium hydroxide solution. The pigment was then filtered employing a Buchner funnel, washed thoroughly three times with distilled water, dried in air, and washed again twice by suspending it in distilled water. Zinc triphosphate must not be dried by heating because the anion undergoes self-hydrolysis, the hydrolysis rate being dependent on the temperature and the pH of the medium. It has been established that at room temperature and pH 5, the half life of the pigment is 10,000 hours (more than a year); but at 80°C it is only five hours.¹³

Characterisation of the zinc triphosphate pigment

The composition of the pigment, prepared in the way previously described, was established by current analytical techniques. The physicochemical characteristics of zinc triphosphate, relevant to paint technology, such as density (ASTM D1475) and oil absorption (ASTM D281), were determined according to standardised procedures. The pH, conductivity, and ionic composition of the aqueous-saturated solution were also obtained.

Evaluation of the inhibitive properties of zinc triphosphate suspensions

The inhibitive properties of the zinc triphosphate pigment were assessed by measuring the corrosion potential of a SAE 1010 steel electrode in the pigment suspension during four hours to detect the formation of any passive film. Then the corrosion potential was measured after 24 hours to see if the system was left protected. Two surface finishes were employed: one of low roughness (mean peak-to-valley height 1.4µm) and the other was obtained by sandblasting (mean peak-to-valley height 21µm). The corrosion potential was measured with a high impedance voltmeter. The saturated calomel electrode (SCE) was used as reference and the electrolyte was a 0.025M sodium perchlorate solution.

Steel polarisation resistance (with IR-drop compensation) was measured in the same pigment suspension and in the supporting electrolyte. The reference electrode was SCE and the counterelectrode a platinum grid. The sweep amplitude was +20mV and the scan rate was 0.166mV.s⁻¹. Measurements were taken employing a Model 273A EG & G Par Potentiostat/Galvanostat plus Softcorr 352 software.

The protective layer formed after 24 hours of exposure to the zinc triphosphosphate pigment suspension was examined by scanning electron microscopy (SEM). The surface amount of iron, phosphorus and zinc was determined by energy dispersive analysis of x-ray (EDXA).

Anodic and cathodic polarisation curves of the SAE 1010 steel electrode, in pigment suspensions in 0.5 M sodium perchlorate solution, were obtained after 24 hours of exposure. The cell employed to carry out these measurements was similar to that employed to determine the polarisation resistance. The sweep began in the vicinity of corrosion potential at a scan rate of 3mV.s⁻¹.

Composition, manufacture and application of paints containing zinc triphosphosphate

The materials used to form the paint films to carry out this research were as follows: a medium oil alkyd (50% linseed oils, 30% o-phthalic anhydride, 8% pentaerythritol and glycerol, and 12% pentaerythritol resinate) and also an epoxy-polyamide resin. The solvent employed in the former case was white spirit while the mixture xylene/methyl isobutyl ketone/butyl cellosolve (13/45/42%w/w) was used for the epoxy paint. It was decided to check the anticorrosive properties of the pigments in solvent-borne paints because their behaviour has been well documented for many years.

Two different contents of zinc triphosphosphate were employed to formulate the paints: 10 and 30%v/v, with respect to the total pigment concentration. Titanium dioxide, barium sulphate and talc were incorporated to complete the pigment formula. On evaluating the initial results, it was noticed that some paints exhibited a low anticorrosive performance. To avoid this difficulty, it was thought to increase the talc content of these paints to improve the barrier effect. Pigments were dispersed in the paint formulation for 24 hours employing a ball mill with a 3.3-litre jar to achieve an acceptable dispersion

degree.¹⁴ The PVC/CPVC relationship was 0.8. The composition of tested paints is shown in Table 1.

SAE 1010 steel panels (15.0 x 7.5 x 0.2cm) were sandblasted to approximately Sa 2^{1/2} (SIS 05 59 00), degreased with toluene, and then brushed up to a thickness of 75 ±5µm. Painted panels were kept indoors for seven days before being tested.

The performance of anticorrosive paints in accelerated and electrochemical tests

A set of three panels was placed in the salt-spray chamber (ASTM B117). Rusting (ASTM D610) and blistering (ASTM D714) degrees were evaluated after 480 and 600 hours of exposure. The adhesion of the coatings to the steel substrate was measured by the cross-cut tape test (ASTM D3359) at the beginning of the test period and after 24, 170 and 720 hours of exposure to the salt-spray chamber.

Another set of panels was placed in the humidity chamber at 38 ±1°C for 400 and 950 hours (ASTM D2247). Rusting and blistering degrees were assessed as described above.

The cells to perform electrochemical measurements were constructed by delimiting 3cm² circular zones on the painted surface by placing an acrylic tube (7.0cm high) on the painted specimen and filling it with the supporting electrolyte (0.5M sodium perchlorate solution). The ionic resistance between the coated steel substrate and a platinum electrode was measured employing an ATI Orion (model 170) conductivity meter at a 1000Hz frequency. The corrosion potential was monitored against a reference electrode (SCE) with a high impedance voltmeter.

The polarisation resistance of painted specimens was determined as a function of immersion time by employing the cell described previously with the SCE as ref-

erence and a platinum grid as the counterelectrode. The voltage scan was +20mV and the scan rate was 0.166mV.s⁻¹. Measurements were taken employing a Model 273A EG & G Par Potentiostat/Galvanostat plus Softcorr 352 software.

Results and Discussion

The chemical analysis of the pigment showed that its composition was as follows: PO₄³⁻: 47.63%, Na¹⁺: 2.05%, Zn²⁺: 24.40%. The mass loss by heating zinc triphosphosphate at 100°C was 22.60% and the further mass loss on ignition at 800°C was 3.32%. According to these results, the stoichiometry of zinc triphosphosphate was found to be Zn₂Na (P₃O₁₀).5H₂O. The density of the pigment was found to be equal to 2.08g/ml and the oil absorption was 0.56ml/g.

The pH value of the pigment suspension was lower than the pH value of a zinc phosphate suspension¹⁵ but this difficulty may be overcome by carefully selecting the complementary pigments. The conductivity of the suspension was rather high (185.2µS) compared with that of zinc phosphate measured under the same conditions.¹⁵ This fact was attributed to the higher solubility of zinc triphosphosphate with respect to zinc phosphate, which resulted in higher amounts of dissolved phosphate anion (5.76ppm) in the saturated solution.¹⁵

The corrosion potential of SAE 1010 steel in the zinc polyphosphate suspension (see Figure 2) moved towards more positive values during the first two hours of immersion to finally descend down to -622mV after 24 hours of exposure; this was slightly higher than the corrosion potential of the blank situation (-650/-700mV), although no corrosion signs were observed on the metal surface. The measurement of the polarisation resistance (with IR-drop compensation) against the blank situation was 8.79 times higher indicating that the zinc

Table 1: Solids in paint composition as percentage by volume

Components	Paints					
	1	2	3	4	5	6
Zinc triphosphosphate	4.4	14.1	14.1	4.4	14.1	14.1
Barium sulphate	24.7	17.9	13.6	24.7	17.9	13.6
Talc	7.9	7.3	13.6	7.9	7.3	13.6
Titanium dioxide	9.3	7.0	5.0	9.3	7.0	5.0
Alkyd resin	53.7	53.7	53.7	-	-	-
Epoxy/polyamide resin (1:1)	-	-	-	53.7	53.7	53.7
Zinc triphosphosphate concentration, %v/v, with respect to the total pigment content	10	30	30	10	30	30

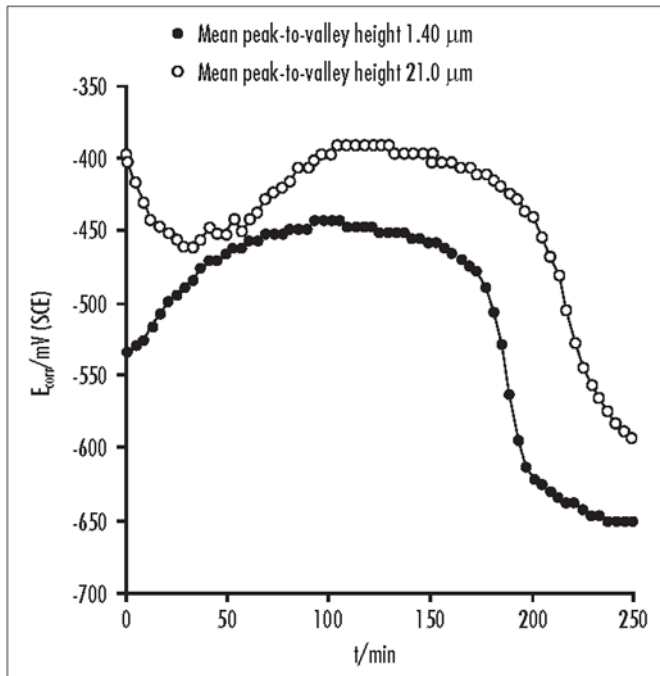


Figure 2: Corrosion potential of SAE 1010 steel panels, as a function of the exposure time, in 0.025M sodium perchlorate solution

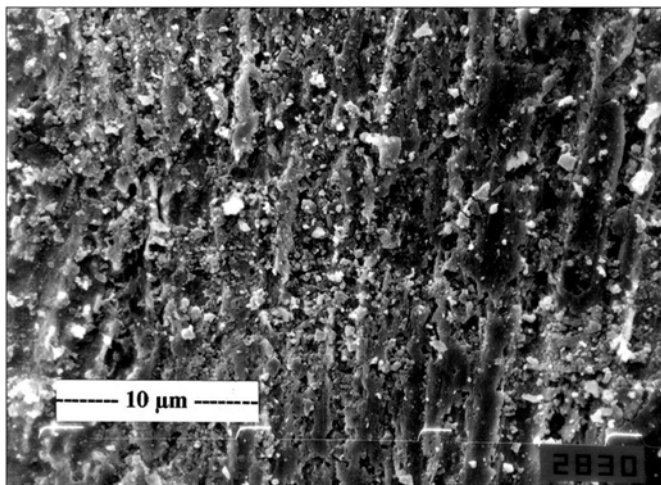


Figure 3: SEM micrograph of the film formed on the steel panel in contact with the zinc triphosphate suspension in 0.025M sodium perchlorate (2000X)

triphosphate pigment formulation has an important effect in decreasing steel corrosion.

A light grey film was formed due to the reaction between the steel and the pigment formulation after 24 hours' exposure. No corrosion signs were detected (see Figure 3). The protective film was examined by SEM and its composition determined by EDXA (energy dispersive x-ray analysis). It was constituted by a rather compact layer in which the superficial amount of zinc was found to be equal to 1.75%, the phosphorus amount was 2.92%, the remainder being iron. It was thought that the presence of this film increased the polarisation resistance which resulted in a lower corrosion rate.

The anodic polarisation curve shows that zinc triphosphate passivated the steel substrate. The critical current density to achieve passivation was lower than that required to passivate steel in the presence of zinc phosphate.¹⁵ The current in the passive region was also smaller, indicating improved protection of the steel substrate (see Figure 4a).

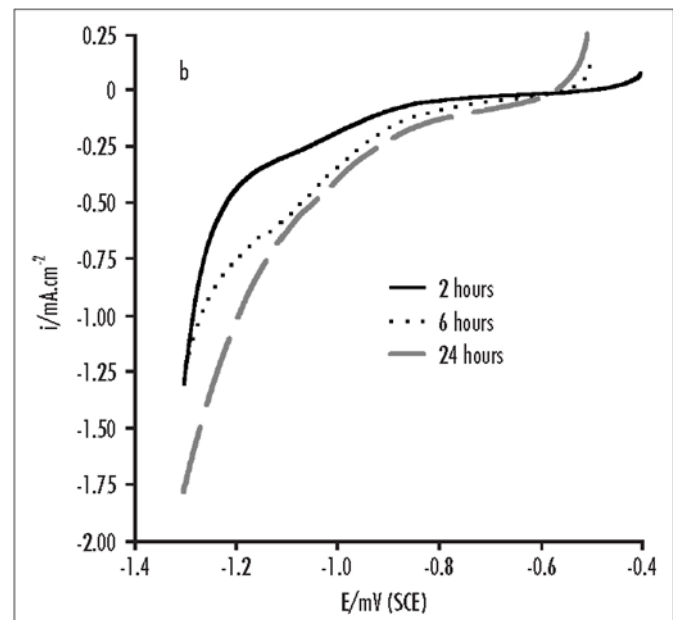
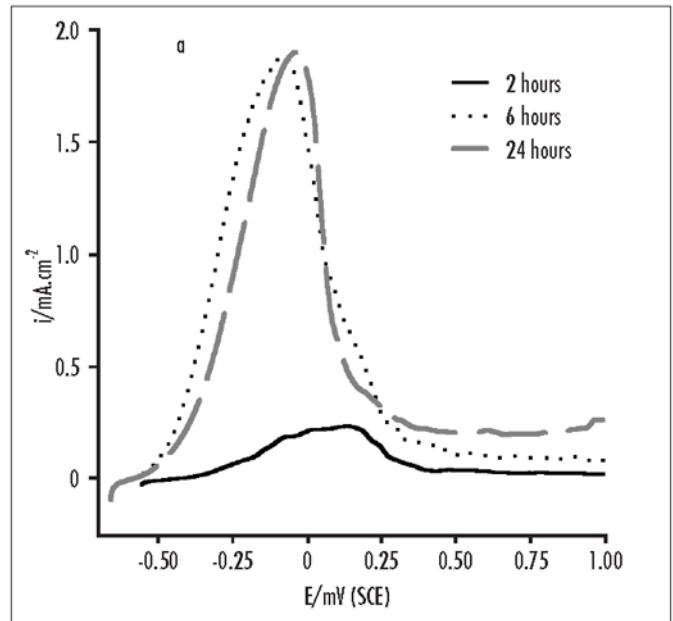


Figure 4: Polarisation curve of the SAE 1010 steel electrode in the zinc triphosphate suspension in 0.5M sodium perchlorate: a) anodic b) cathodic

The oxygen-reduction reaction occurred at more negative potentials as time elapsed, pointing out that the cathodic reaction needed greater applied potentials to start. The reduction of corrosion products formed on the electrode surface was clearly observed, after six hours of exposure, at potentials close to $-0.95V$.

The performance of anticorrosive paints in accelerated tests

With respect to alkyd paints, the best anticorrosive behaviour in the salt-spray test was observed in the case of the paint with the lowest zinc triphosphate pigment content (see Table 2, Paint 1). Neither signs of corrosion nor blistering were observed in panels coated with this paint after 600 hours of exposure. The increase in the zinc triphosphate pigment content did not lead to better results as observed with calcium triphosphate.¹⁶ This was thought to be due to the higher solubility of triphosphates compared with zinc phosphates. Increasing the amount of talc in the case of the alkyd paint containing 30%v/v of the zinc triphosphate pigment resulted in smaller blistering (see Table 2, Paint 3).

Table 2: Rusting degree (ASTM D610) and blistering degree (ASTM D714) of the painted panels in the salt spray cabinet

Paint	Time (hours)			
	480 hours		600 hours	
	Rusting	Blistering	Rusting	Blistering
1	10	10	10	10
2	9	6D	8	6D
3	9	8D	8	8D
4	8	10	7	8F
5	10	10	9	10
6	10	10	10	10

The behaviour of the epoxy paint containing 10% of the zinc triphosphosphate pigment (see Table 2, Paint 4) was poorer than the anticorrosive performance of alkyds. The paint containing 30% of zinc triphosphosphate pigment by volume showed a good behaviour which was improved by increasing the talc content (see Table 2, Paint 6). It was considered that there was incompatibility between the zinc triphosphosphate pigment and the epoxy resin because of the lower ionic resistance values observed for these paints, as it will be pointed out later. On the other hand, a synergistic effect between the alkyd resin and zinc cation may enhance the anticorrosive behaviour of these paints which showed a good anticorrosive performance. It will be seen from electrochemical measurements that the protection afforded by these paints rested on the inhibitive properties of the zinc triphosphosphate pigment due to the relatively low barrier effect observed for most coated panels.

The performance of paints pigmented with zinc triphosphosphate, in an accelerated test, has been shown to be clearly superior to the behaviour of similar paints containing aluminium triphosphosphate.¹²

The adhesion of paints (see Table 3) before entering the salt-spray cabinet was 5B, the higher classification that the standard ASTM D3359 gives in the corresponding scale. After a day of exposure, only paints 2 and 3 diminished their adhesion, losing it almost completely after seven days of exposure. The alkyd paint with a higher talc content (see Table 1, Paint 3) showed lower adhesion while no significant differences were observed in the case of epoxies.

Table 3: Adhesion (ASTM D3359) of the painted panels in the salt-spray cabinet

Paint	Time (hours)			
	0	24	170	720
1	5B	5B	5B	3B
2	5B	4B	1B	–
3	5B	2B	–	–
4	5B	5B	5B	5B
5	5B	5B	5B	5B
6	5B	5B	5B	5B

It must be pointed out that paints 2 and 3, in spite of losing metal/coat adherence after 24 hours, still showed a good rating in the salt-spray test (see Table 2). This led to the conclusion that the zinc triphosphosphate pigment formulation actually inhibited steel corrosion.

The alkyd paint with the lowest zinc triphosphosphate content blistered in the humidity chamber (see Table 4 Paint 1) during the first week, keeping the blistering degree steady during one

Table 4: Corrosion degree (ASTM D610) and blistering degree (ASTM D714) of the painted panels in the humidity chamber

Paint	Time (hours)			
	400		950	
	Corrosion	Blistering	Corrosion	Blistering
1	10	6MD	10	6MD
2	7	4MD	–	–
3	10	10	10	10
4	10	10	10	10
5	10	10	10	10
6	10	10	10	10

month. No rust spots appeared during this period. The alkyd paint with a higher pigment concentration blistered after 400 hours and showed a rusting degree of 7. Epoxy paints did not blister after 950 hours and no signs of corrosion were detected after this time had elapsed. Paint 5 continued to protect the steel substrate after 1900 hours of exposure exhibiting a rusting degree equal to 9, but no blisters were present. A reproducible behaviour was noticed again with respect to the zinc triphosphosphate pigment content; while alkyd paints performed better with the lowest zinc triphosphosphate pigment content, epoxy paints remained rather insensitive to the change in pigment content in the 10 to 30%v/v range.

The performance of anticorrosive paints in electrochemical tests

As expected, alkyd paint did not show an important barrier effect (see Figure 5), although paint containing 10%v/v of the pigment showed certain barrier properties which were quickly lost after the first day of immersion. The incorporation of higher amounts of talc did not introduce substantial improvements in coating resistance to water and ion permeation (Figure 5, Paint 3). An increase in the pigment content impaired the anticorrosive behaviour of the coating.

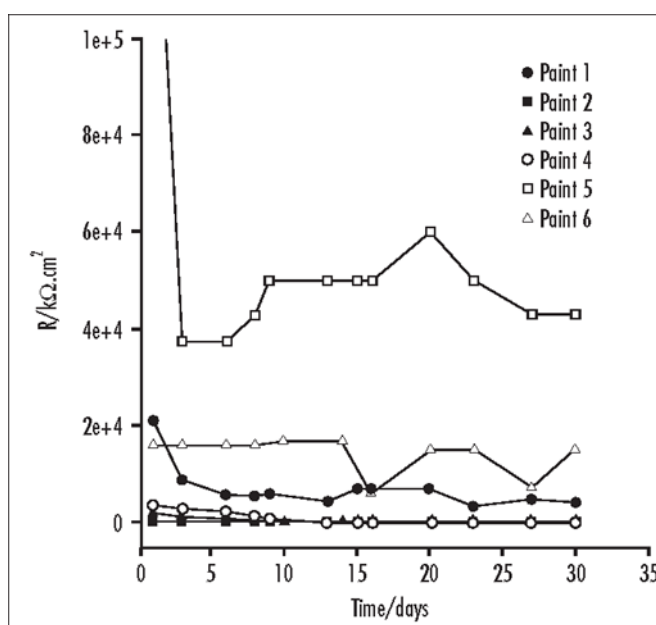


Figure 5: Ionic resistance of painted steel as a function of the exposure time in 0.5M sodium perchlorate solution

The variation of the ionic resistance as a function of time (see Figure 5) indicated that only the epoxy paint containing 30%v/v

of the zinc tripolyphosphate pigment showed a certain barrier effect which was maintained during the test period. When the zinc tripolyphosphate pigment content decreased to 10%, the barrier effect was notably impaired. The incorporation of talc did not improve the barrier properties of the coatings. According to these results, it would seem that a higher pigment content would be desirable in the case of epoxy paints.

The corrosion potential of steel coated with paints formulated with zinc tripolyphosphate (see Figure 6) was displaced, as a general rule, to more positive values during the first week of immersion. The exception was the epoxy paint containing the lowest zinc tripolyphosphate pigment content (Paint 4), which was quickly displaced to negative values indicating a premature coating failure in protecting the steel.

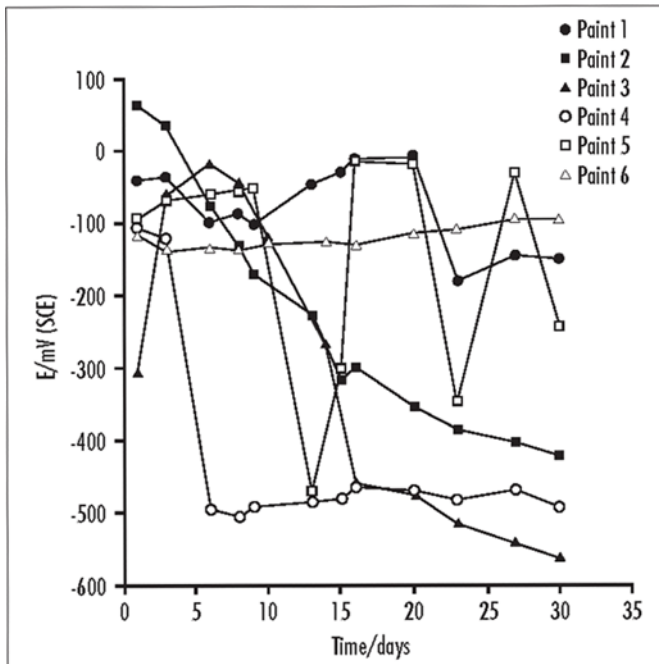


Figure 6: Corrosion potential of painted steel as a function of the exposure time in 0.5M sodium perchlorate solution

The alkyd paint containing 10%v/v zinc tripolyphosphate showed the best behaviour revealing the protective properties of the pigment formulation (Paint 1); this behaviour was maintained until the end of the test indicating full protection of the steel substrate. The corrosion potential of the other alkyd paint changed towards a more negative potential but a certain degree of protection was also noticed. The increase of the talc content improved coating performance during the first fortnight of immersion (Paints 3 and 6). Considering that the barrier effect was almost negligible, the protection was considered to depend upon the inhibitive characteristics of the zinc tripolyphosphate pigment.

The corrosion potential of epoxy paints showed a tendency to change towards negative values after a few days of immersion, but a strong tendency to repassivation was noticed in the case of the epoxy paint with the highest anticorrosive pigment content. The incorporation of talc seemed to be beneficial because it kept the steel potential in the vicinity of -100mV (SCE) during the whole test period.

The response of steel coated with alkyd paints to linear polarisation perturbation depended on the pigment content. The polarisation resistance of the paint containing 10% by volume of the zinc tripolyphosphate pigment could not be measured due to the high ionic resistance. In this case a linear response

indicating ohmic control may be obtained, or very low corrosion rates (which were difficult to measure with the technique employed) would be measured. For higher zinc tripolyphosphate pigment contents the polarisation resistance was slightly higher than the ionic resistance indicating a certain inhibition of the corrosion process. However, as a consequence of the inhibitive properties of the zinc tripolyphosphate pigment, the polarisation resistance may experience sudden changes and become more than 100 times higher than the ionic one. The polarisation resistance of epoxy paints could not be measured because of the high ionic resistance of the coating.

Conclusion

Zinc tripolyphosphate is considered to inhibit steel corrosion by generating a protective layer mainly composed of non-expansive iron oxides.

The best anticorrosive behaviour in alkyd paints was observed with the lowest zinc tripolyphosphate pigment content (10% by volume).

Epoxy paints were less sensitive to the increase in zinc tripolyphosphate pigment content from 10%v/v to 30%v/v. Better anticorrosive performance was observed with the highest zinc tripolyphosphate pigment content (30% by volume).

The incorporation of talc in the formulation improved the anticorrosive performance of zinc tripolyphosphate. Talc also improved blistering resistance in alkyd paints. These improvements are considered to be due to an improved barrier effect.

Good correlation was observed between accelerated and electrochemical tests.

Acknowledgements

The authors are grateful to CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) and UNLP (Universidad Nacional de La Plata) for their sponsorship to conduct this research. The authors also thank Raúl Pérez for the analytical determinations, and POLIDUR SA for providing the alkyd resin to carry out this research.

References

1. Meyer G, 'Über Zinkphosphat und Bariumchromat als moderne Korrosionsinhibitoren', *Farbe & Lack*, **69**, (7), 528–32, 1963
2. Barraclough J and J B Harrison, 'New leadless anti-corrosive primers', *JOCCA*, **48**, (4), 341–55, 1965
3. Romagnoli R and V F Vetere, 'Non-pollutant corrosion inhibitive pigments: zinc phosphate, a review', *Corrosion Review*, **13**, (81), 45–64, 1995
4. Gerhard A and A Bittner, 'Second generation phosphate anti-corrosive pigments. Formulating rules for full replacement of new anti-corrosive pigments', *JCT*, **58**, (740), 59–65, 1986
5. Fragata F de L and J E Dopico, 'Anticorrosive behaviour of zinc phosphate in alkyd and epoxy binders', *JOCCA*, **74**, (3), 92–7, 1991
6. Hare C H, 'Anatomy of paints: Inhibitive primers to passivate steel', *J Protective Coat & Linings*, **7**, (10), 61–7, 1990
7. Bittner A, 'Advanced phosphate anticorrosive pigments for compliant primers', *JCT*, **61**, (777), 14–118, 1989
8. del Amo B, R Romagnoli and V F Vetere, 'Study of the anticorrosive properties of zinc phosphate and zinc molybdophosphate in alkyd paints', *Corrosion Review*, **14**, (1–2), 121, 1996

9. Chromy L and E Kaminska, 'Non-toxic anticorrosive pigments', *Prog Org Coat*, **18**, (4), 319–24, 1990
10. Noguchi T, J Nahono, M Kabayashi, M Nagita, M Kinugasa and M Murakami, 'Studies on the anticorrosive properties of aluminium triphosphate pigments', *PPCJ*, **174**, (4133), 888–91, 1984
11. Takashashi M, 'Characteristics and applications of the triphosphate as a special chemical', *PPCJ*, 281–4, 18th April, 1984
12. Deya M C, V F Vetere, R Romagnoli and B del Amo, 'Aluminum triphosphate pigments for anticorrosive paints', to be published in *Pigment & Resin Technology*
13. Toy A D F, 'Phosphorus', *Comprehensive Inorganic Chemistry*, **3**, A F Trotman-Dickenson (ed), Pergamon Press, NY, 1973
14. Giúdice C A, J C Benítez and V J D Rascio, 'Study of variables which affect dispersion of antifouling paints in ball mills', *JOCCA*, **63**, (4), 153–8, 1980
15. Blustein G, B del Amo and R Romagnoli, 'The influence of the solubility of zinc phosphate pigments on their anticorrosive behaviour', *Pigment Resin Tech*, **29**, (2), 100–7, 2000
16. Vetere V F, M C Deya, R Romagnoli and B del Amo, 'Calcium tripolyphosphate: an anticorrosive pigment for paints', *JCT*, **73**, (917), 57–63, 2001