

# ZINC MOLYBDENUM PHOSPHATE: AN EFFECTIVE ANTICORROSIVE PIGMENT FOR SOLVENT AND WATER BORNE PAINTS

B. del Amo<sup>1</sup>, G. Blustein<sup>2</sup>, M.C. Deyá<sup>3</sup>, R. Romagnoli<sup>1,4</sup>

<sup>1</sup>*Investigador CONICET*, <sup>2</sup>*Becario CIC*, <sup>3</sup>*Becario CONICET*

<sup>4</sup>*Profesor Facultad de Ciencias Exactas, UNLP.*

*CIDEPINT - Centro de Investigación y Desarrollo en Tecnología de Pinturas, Calle 52 e /121 y 122. (1900) La Plat., Argentina  
Fax 54 0221-427 1537, E-mail: estelectro@cidepint.gov.ar.*

## ABSTRACT

The anticorrosive properties of two commercially available phosphate pigments, with different molybdenum content in their composition, have been investigated. The anticorrosive properties of the pigments were assessed by electrochemical techniques in pigment suspensions and then in solvent and water-borne paints. The paints contained 30% by volume of anticorrosive pigment, with respect to the total pigment content.

The anticorrosive performance of paints formulated with different binders – alkyd, epoxy and water-borne epoxy – has been evaluated by accelerated (salt spray cabinet and humidity chamber) and electrochemical tests (corrosion potential and ionic resistance).

It was found that paints formulated with both pigments behaved satisfactorily in accelerated tests and both provided very good anticorrosive protection to steel. The pigment with the highest molybdenum content showed a better performance in water-borne paints.

**Key words:** corrosion, zinc molybdenum phosphate, solvent borne paints, water borne paints, accelerated tests, electrochemical tests.

## INTRODUCTION

Organic coatings are effective in protecting steel against corrosion in aggressive environments. Classical anticorrosive paints normally employ inhibitors based on hexavalent chromium or lead compounds. These compounds are being restricted because they contaminate the environment and cause health problems in humans.

Among many non-toxic anticorrosive pigments, zinc phosphate became the leading substitute for chromate and lead based pigments. Although it generally gives good results, in certain cases it proved to have lower performance than zinc chromate /1-5/. As a consequence, a second generation of modified zinc phosphate pigments was introduced in the eighties /6,7/. One of these new phosphate pigments is that termed "zinc molybdenum phosphate". Zinc molybdenum phosphate is prepared from zinc phosphate added with zinc molybdate up to 1% (expressed as  $\text{MoO}_3$ ) /8/. Synergistic effects may be expected when molybdate is used with other common inhibitors such as phosphate /9,10/. This fact has important technical and commercial implications, even in paint technology; specially taking into account that molybdate is a fairly costly inhibitor. The phosphate anion, produced by slight solubilization of the inhibitor, might act cathodically or anodically /11,12/ supplementing the anodic effect of molybdate. Apart from phosphate, the other active inhibitive species of the pigment is the molybdate ion ( $\text{MoO}_4^{2-}$ ), which is said to re-passivate corrosion pits in steel /13-15/.

The objective of this paper was to study the anticorrosive performance of two phosphate pigments containing different amounts of molybdenum in their composition. The pigments were employed to formulate solvent and water-borne paints, whose efficiency was evaluated by accelerated and electrochemical tests. Both pigments worked successfully in all tests carried out in this research.

## EXPERIMENTAL PROCEDURES

### Pigment characterisation

The chemical composition of the pigments employed in this research was established by analytical procedures. The composition, and pH of the aqueous extract of the pigments were also determined.

## Evaluation of the inhibitive properties of pigment suspension

The inhibitive properties of the pigments were evaluated, in the first instance, by measuring the corrosion potential of an AISI 1010 steel electrode in the corresponding pigment suspension, during 24 hours. The saturated calomel electrode (SCE) was used as reference and the electrolyte was a 0.025 M sodium perchlorate solution.

The protective layer formed on steel, after 24 hours of exposure to the pigment suspension, was examined by scanning electron microscopy (SEM). The surface amount of iron, phosphate and molybdenum was determined by Energy Dispersive X-ray Analysis (EDXA).

Steel polarisation resistance, in the same pigment suspension, was also measured in comparison with bare steel. Steel polarisation resistance was also measured in solutions containing sodium chloride, to differentiate better the behaviour of both pigments. The reference electrode was SCE and the counterelectrode was a platinum grid. The sweep amplitude was  $\pm 20$  mV, starting from the corrosion potential, at a scan rate of 0.166mV/s. Measurements were taken employing model 273A EG&G PAR Potentiostat/Galvanostat plus SOFTCORR 352 software.

Steel corrosion rate was obtained from Tafel plots in pigments suspensions in 0.5 M sodium perchlorate solution. The electrochemical cell was that described in the previous paragraph and the electrode potential was scanned  $\pm 250$  mV from the open circuit potential. Anodic and cathodic polarisation curves of a steel electrode in the same pigments suspensions were also obtained at different exposure times. The sweep began in the vicinity of the corrosion potential, at a scan rate of 3 mVs<sup>-1</sup>.

## Composition, manufacture and application of paints

### *Solvent borne paints:*

The materials used to form the paint films to carry out this research were a medium oil alkyd resin (50% linseed and tung oil, 30% o-phthalic anhydride, 8% pentaerythritol and glycerol and 12% pentaerythritol resinate) and a bisphenol A epoxy resin / polyamide (1/1 ratio by volume). The solvent mixture employed for alkyd paints was white spirit while xilene/methyl isobutylketone/butyl cellosolve (13/45/42 % w/w) was used for epoxy paints. The alkyd paints were identified with letter A and the epoxy ones with letter E.

The anticorrosive pigment content was 30 % by volume, with respect to the total pigment content. Titanium dioxide, barium sulphate and talc were incorporated to complete the pigment formula. Pigments were dispersed in the vehicle employing a ball mill with a 3.3 litre jar, during 24 hours, to achieve an acceptable degree of dispersion /16/. The composition of tested paints is shown in Table I.

**Table I**  
Composition of the paints expressed as % by volume of solids

Components	Solvent borne paint	Water borne paint
Anticorrosive pigment	12.6	6.0
Titanium dioxide	4.8	3.9
Barium sulphate	12.2	4.2
Talc	12.2	3.9
Alkyd resin or Epoxy resin / Polyamide resin (1/1 ratio)	58.2	--
Bisphenol A and Bisphenol F / Polyamidoamine 1/1.2 ratio	--	80.0
Additives	---	2.0
Anticorrosive pigment / total pigment (v / v)	30	30

***Water-borne paints:***

The resin used to formulate these paints was an epoxy one, based on a mix of bisphenol A and bisphenol F. The curing agent which acted, at the same time, as the emulsifier, was a modified polyamidoamine with 50% of solids. The resin/hardener ratio was 100/120 parts by weight and demineralized water (pH 7) was used as solvent. The selected PVC value was 20% in order to enhance the barrier effect of the paints (Table I).

The anticorrosive pigment content was 30% by volume, with respect to the total pigment content. In order to complete the pigment formula, titanium dioxide, barium sulphate, talc and mica were incorporated. Mica was incorporated due to its barrier properties and to reduce the degree of "flash rusting" /17/.

Paint manufacture was carried out employing high-speed dispersing equipment. Preliminary tests showed the advantage of incorporating pigments into the hardener instead of the resin, due to the relatively high viscosity of the hardener. Therefore, water was added first and then the pigments, in accordance with their increasing oil absorption. Mica was incorporated at the end of the elaboration procedure to avoid the break-up of laminar particles.

AISI 1010 steel panels (15.0 x 7.5 x 0.22 cm) were sandblasted to Sa 2 172 (SIS 05 59 00), degreased with toluene and then painted by brush up to a thickness of  $80 \pm 5 \mu\text{m}$ . Painted panels were kept indoors for 14 days before testing.

### **The performance of anticorrosive paints through accelerated and electrochemical tests**

A set of 3 panels, for each paint, were placed in the salt spray chamber (ASTM B 117) to evaluate the degree of rusting (ASTM D 610) after 1000 and 2000 hours of exposure, respectively. Another set of panels was exposed in the humidity chamber at  $38 \pm 1^\circ\text{C}$  (ASTM B 2247) for 850 hours. The degree of blistering was established according to the ASTM D 714 standard specification.

The electrochemical cells were constructed by delimiting  $3 \text{ cm}^2$  circular zones on the painted surface. An acrylic tube, 7.0 cm high, was placed on the specimen and filled with the electrolyte (0.5M sodium perchlorate solution). The corrosion potential of coated steel was measured employing a saturated calomel electrode, as reference, and a high impedance voltmeter.

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

## **RESULTS AND DISCUSSION**

### **Pigment characterisation**

According to data presented in Table II, pigment 1 contained 72.0% of zinc phosphate and pigment 2 contained a similar amount (71.6%). Both pigments also contained zinc oxide, pigment 1: 8.8 % and pigment 2: 15.0 %. Small amounts of molybdenum, probably as zinc molybdate, were added in

**Table II**  
Pigments composition

	Solid pigment			Density (g/cm <sup>3</sup> )	Aqueous extract		
	Composition (% p/p)				Solubility (ppm)		pH
	MoO <sub>3</sub>	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	ZnO		Zn <sup>2+</sup>	PO <sub>4</sub> <sup>3-</sup>	
Pigment 1	0.32	72.0	8.80	3.2	4.3	<0.1	7.80
Pigment 2	0.92	71.6	15.0	4.2	7.8	<0.1	7.40

each case; pigment 2 had a higher molybdenum content.

The phosphate content in the aqueous extract (Table II) was lower than 0.1 ppm, this value being the sensibility of the spectrophotometric technique employed in this case. The phosphate content is similar to that reported in the literature for zinc molybdenum phosphate /6/. The zinc content was lower than the value consigned in previous research and only slightly higher, in the case of pigment 2, than the value determined for zinc phosphate /6/. The pH of the aqueous extract of both pigments is quite similar and higher than 7, the pH at which steel passivation is said to start /18/.

### Evaluation of the inhibitive properties of pigment suspension

Electrochemical tests revealed that the pigments protected steel against corrosion. Corrosion potential, measured after 4 hours exposure, corresponded to that of passivated steel and was found to be equal to  $\sim -400$  mV, as an average, for pigment 1 while more noble values ( $\sim -240$  mV) were observed for pigment 2 (Fig. 1). The corrosion potential of bare steel comprised between  $-650$  and  $-750$  mV.

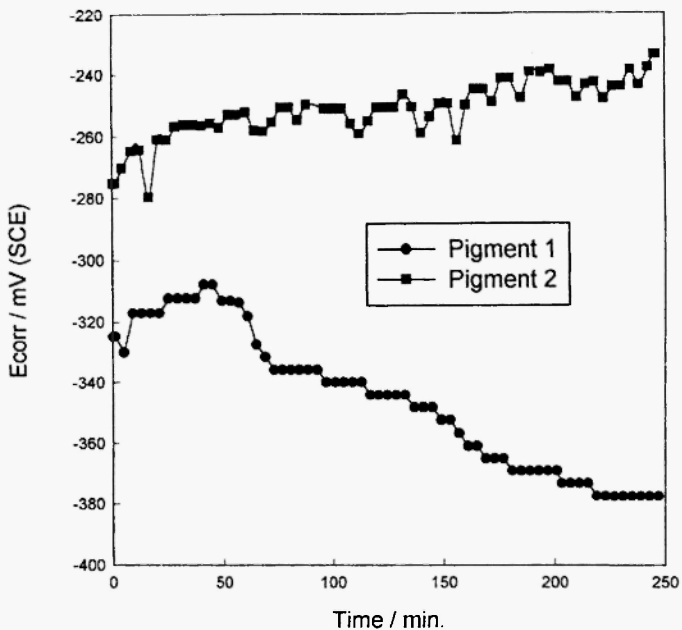


Fig. 1: Corrosion potential of SAE 1010 steel panels, as a function of the exposure time, in 0.025 M sodium perchlorate solution.

The protective layer formed on steel, at open circuit potential, was observed by SEM. Both pigments produced the same protective layer; it appeared as a compact film on the entire exposed surface. The film composition, determined by EDAX, showed that it was constituted by non expansive amorphous ferrous oxide. No molybdenum was found in the film.

The polarisation resistance values (Table III) showed that there are no important differences between both pigments, although in the presence of chloride pigment 2 seemed to be more efficient than pigment 1 in restraining corrosion. This fact may be attributed to the higher molybdenum content of pigment 2 /9/. This fact confirmed that molybdenum has an important role in corrosion processes induced by chloride ions. Steel polarisation resistance in the presence of both pigments was much higher than that of the blank; indicating an important inhibition of the corrosion of the metallic substrate.

**Table III**  
Steel polarisation resistance in aqueous pigments suspensions

Electrolytic medium	Rp ( $k\Omega \cdot cm^2$ )		Rp / Rp <sub>Blank</sub>	
	1	2	1	2
Pigment 1	46.4	2.9	273	19.5
Pigment 2	41.8	9.7	246	64.6
Supporting electrolyte	0.17	0.15	1	1

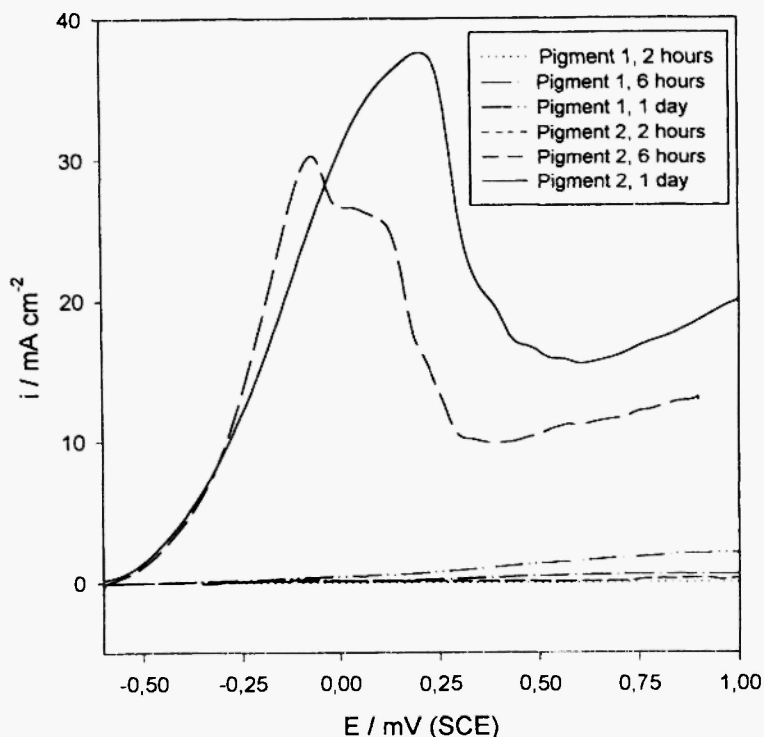
1. Pigment suspension in 0.025 M NaClO<sub>4</sub>
2. Pigment suspension in 0.025 M NaClO<sub>4</sub>+0.0025 M NaCl

The corrosion rate of steel in pigment suspensions was obtained from Tafel plots, at different exposure times. No significant differences were observed between the pigments after 2 hours of exposure (Pigment 1: 6.6  $\mu A \cdot cm^{-2}$  and Pigment 2: 6.8  $\mu A \cdot cm^{-2}$ ). After 6 hours, the corrosion rate of steel in contact with pigment 2 increased (9.0  $\mu A \cdot cm^{-2}$ ) while the other remained almost constant. Finally, after 1 day of exposure, the corrosion rate of steel in contact with pigment 2 was lower (12.7  $\mu A \cdot cm^{-2}$ ) than the corrosion rate of steel immersed in pigment 1 suspension (21.6  $\mu A \cdot cm^{-2}$ ). It seemed that at long exposure times pigment 2 had a better anticorrosive performance.



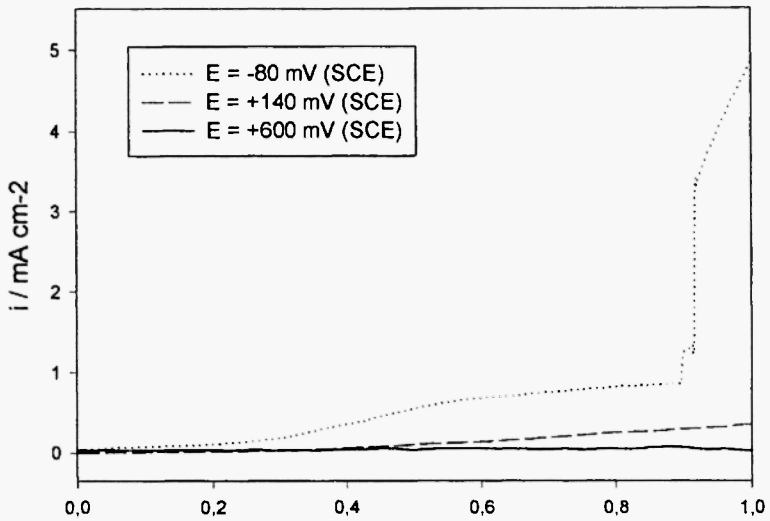
The anodic polarisation curves (Fig. 2) showed that steel oxidation was inhibited in the presence of pigment 1. Pigment 2 also inhibited corrosion during the first hours of immersion. The current density in the passive zone is lower than that obtained with pigment 1, as was revealed by the potential step experiments performed at 600 mV (SCE) (Fig. 3). However, as time elapsed the critical current density for passivation increased significantly for pigment 2 with respect to pigment 1, although peak potentials in the case of pigment 2 moved to more positive values.

The oxygen reaction current, for both pigments (Fig. 4), seemed to be lower than the value obtained with AISI 1010 steel in the supporting electrolyte ( $\sim 125 \mu\text{A}\cdot\text{cm}^{-2}$ ), reported in previous research [19]. As a consequence, the presence of the pigments decreased the oxygen reduction on the steel surface, possibly by blocking the active sites with zinc compounds.



**Fig. 2:** Anodic polarisation curves of the SAE 1010 steel electrode in the pigments suspensions in 0.5 M sodium perchlorate, at different exposure times.

Pigment 1



Pigment 2

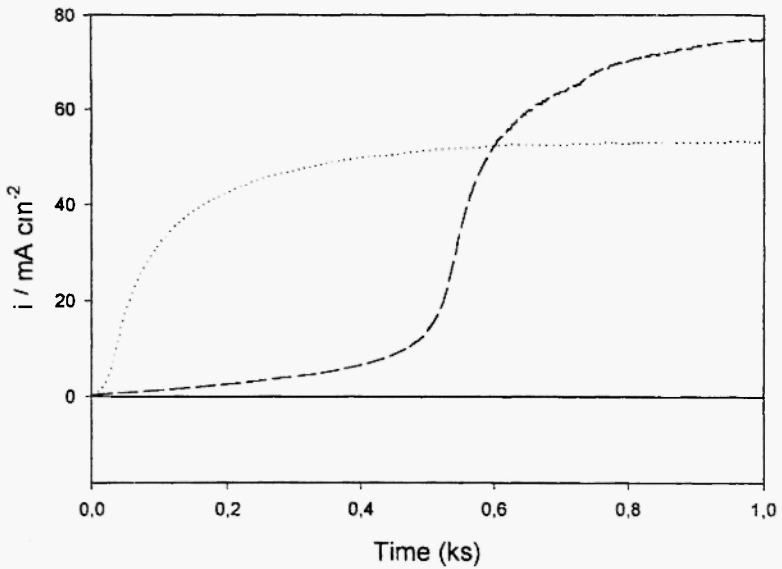
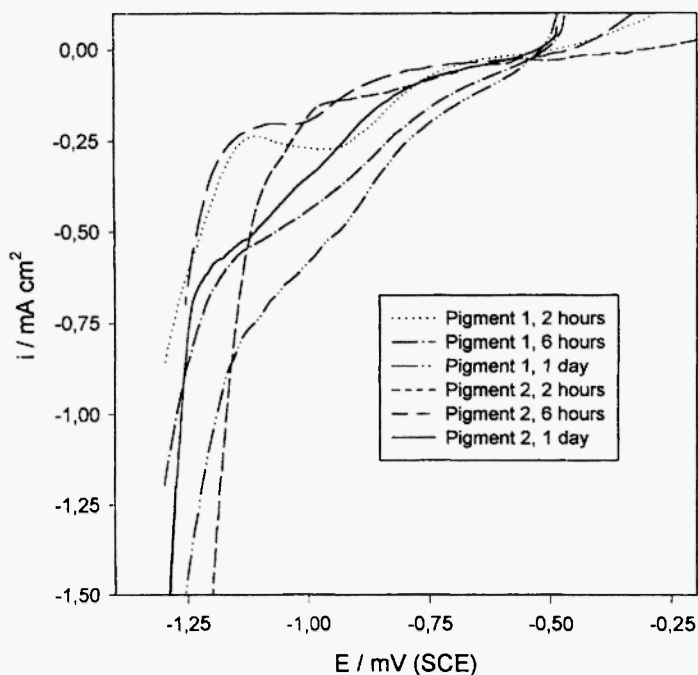


Fig. 3: Potentiostatic transients of the SAE 1010 steel electrode in the pigments suspensions in 0.5 M sodium perchlorate.



**Fig. 4:** Cathodic polarisation curve of the SAE 1010 steel electrode in the pigments suspensions in 0.5 M sodium perchlorate at different exposure times.

### The performance of anticorrosive paints through accelerated tests

The results obtained in the salt spray test (ASTM B 117), which involved the exposure to a very aggressive environment, showed that paints, independently of the pigment, exhibited a very high anticorrosive efficiency. No differences were found between the pigments after the stipulated exposure time, 2000 hours; only alkyd paints blistered and the degree of blistering finally was the same (6F) for both pigments (Table IV).

In the humidity chamber (Table IV), only blisters of small size and low surface density were detected on alkyd paints (8F). Solvent borne epoxy paints did not show blistering after 860 hours of exposure while the water borne epoxy paint, containing pigment 1, showed small blisters with a relatively high density (8D). No corrosion signs were observed under the blisters due to the inhibitive properties of the pigments.

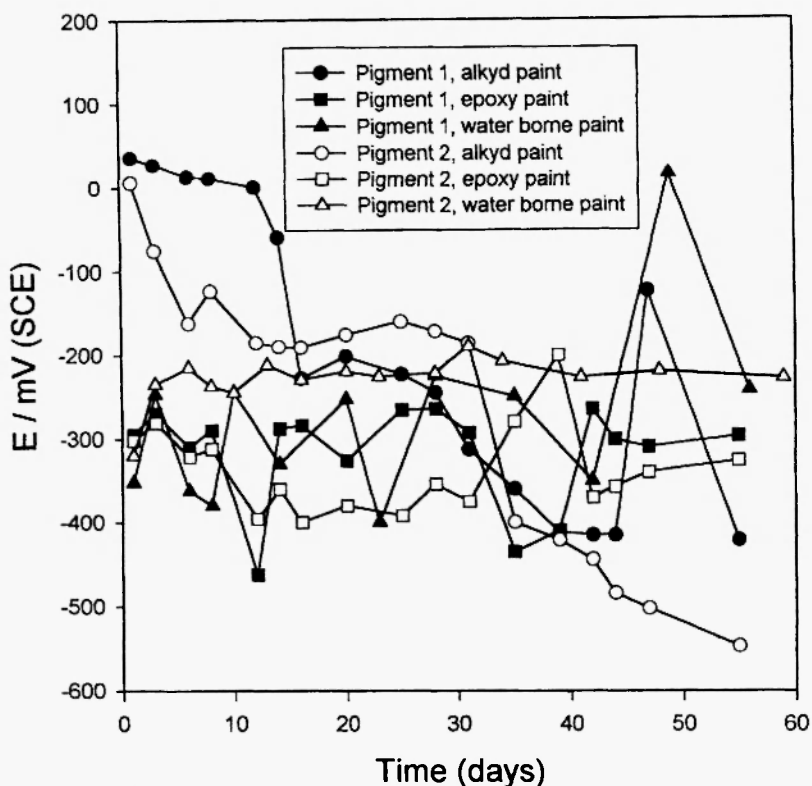
These pigments exhibited a slightly better anticorrosive performance than that reported for zinc phosphate in previous research /20/.

**Table IV**  
Rusting degree and blistering after exposure of painted panels in the salt fog and humidity chambers

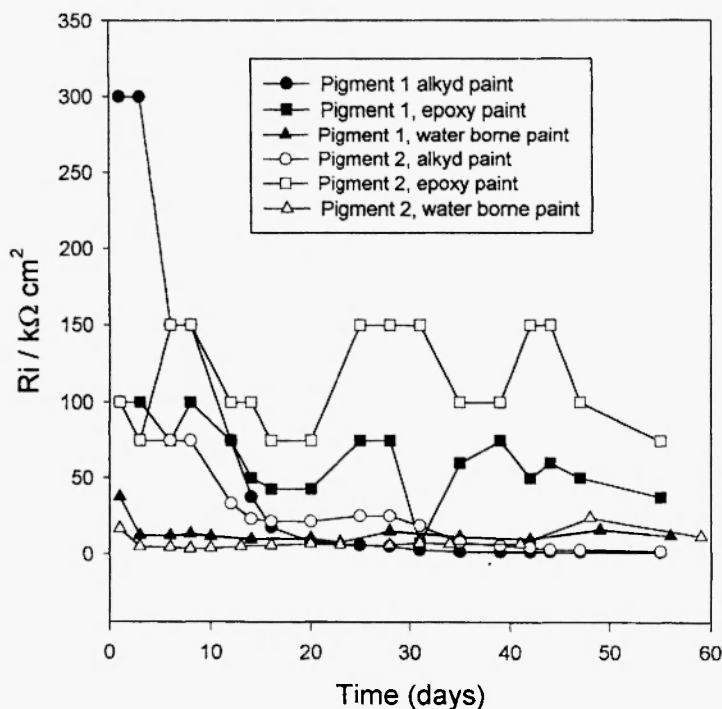
Paint	Salt fog chamber				Humidity chamber	
	1000 hours		2000 hours		860 hours	
	Rusting	Blistering	Rusting	Blistering	Rusting	Blistering
A1	10	10	9	6F	10	8F
A2	9	8F	9	6F	10	8F
E1	10	10	10	10	10	10
E2	10	10	10	10	10	10
Eaq.1	10	10	10	10	10	8D
Eaq.2	10	10	10	10	10	10

Corrosion potential values of painted steel comprised, on average, between  $-150$  and  $-420$  mV. This fact revealed that both paints provided good anticorrosive protection. Alkyd paints exhibited very high corrosion potential values at the beginning of the test period. However, this protective effect was lost after 10-12 days and they showed the worst anticorrosive behaviour at the end of the immersion period. Although epoxy paints showed more negative potentials at the beginning of the test period, they provided a better long term anticorrosive protection. Corrosion potential measurements showed an oscillating behaviour which was attributed to the alternation of the corrosion/passivation process. There are no significant differences between the two pigments in solvent borne paints. Results in this test seemed to depend on the resin type more than on the molybdenum content.

The difference between the two pigments could be appreciated in water borne paints. The paint pigmented with Pigment 2 maintained an almost



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



**Fig. 6:** Ionic resistance of painted steel as a function of the exposure time in 0.5 M sodium perchlorate.

constant potential which fluctuated slightly around  $\sim -220$  mV while the paint containing Pigment 1 fluctuated around  $\sim -400$  mV, exhibiting many oscillations during the immersion period and a strong shifting to very positive potentials after 7 weeks of immersion, to finally decay close to  $-200$  mV.

The alkyd paint pigmented with pigment 1 showed very high ionic resistance values at the beginning of the immersion period which indicated an important barrier effect. The other alkyd paint also showed a barrier effect but, in both cases, it began to decrease after 10 days of immersion and was finally lost. The highest ionic resistance values during the whole test period were observed, obviously, for the epoxy paints which maintained an acceptable barrier effect ( $R_i > 10^6 \Omega \cdot \text{cm}^2$ ) during the entire test period. The ionic resistance of the paints pigmented with Pigment 2 was higher than that of the paint pigmented with Pigment 1. Water borne paints did not provide a barrier to water, oxygen and ion diffusion. However, these paints showed an excellent anticorrosive performance which may be attributed to the inhibitive

properties of the anticorrosive pigments; moreover, the anticorrosive efficiency of the pigments was directly related to its molybdenum content.

### CONCLUSIONS

1. Commercial “zinc molybdenum phosphate” pigments contain low amounts of Mo; typically < 1%. They also contain zinc hydroxide which surely influences positively the anticorrosive properties of the pigment.
2. “Zinc molybdenum phosphate” pigments do inhibit steel corrosion significantly, as was revealed by electrochemical tests.
3. The differences between the two pigments were better appreciated in the presence of chlorides.
4. All paint showed excellent anticorrosive performance in the salt spray and humidity chambers, during the test period.
5. The differences in the anticorrosive performance of both pigments could be appreciated in water borne paints while in the other cases the behaviour seemed to be regulated more by the resin, which levels off the differences between the pigments.
6. It is thought that an increase in the molybdenum content could lead to better results but further research in this field must be conducted in the near future.

### AGKNOWLEDGEMENTS

The authors are grateful to CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), CIC (Comisión de Investigaciones Científicas de la Provincia de Buenos Aires) and UNLP (Universidad Nacional de La Plata) for their sponsorship in carrying out this research. to Tech. Raúl Pérez for the analytical determination and to Polidur San Luis S.A.I.C. for providing the alkyd resin.

### REFERENCES

1. G. Meyer, “Über Zinkphosphat und Bariumchromat als moderne Korrosionsinhibitoren”, *Farbe + Lack*, **69** (7), 528-532 (1963).

2. G. Meyer, "Moderne weiße Inhibitorpigmente und deren Kombinationen in Anstrichsystemen", *Farbe+Lack*, **71** (2), 113-118 (1965).
3. J. Barraclough, J.B. Harrison, "New leadless anti-corrosive primers", *JOCCA*, **48** (4) 341-355 (1965).
4. F. de L. Fragata, J.E. Dopico, "Anticorrosive behaviour of zinc phosphate in alkyd and epoxy binders", *JOCCA*, **74** (3), 92-97 (1991).
5. R. Romagnoli and V.F. Vetere: "Non pollutant corrosion inhibitive pigments: zinc phosphate, a review", *Corrosion Reviews*, **13** (1), 45-64 (1995).
6. A. Bittner, "Advanced phosphate anticorrosive pigments for compliant primers", *JCT*, **61** (777), 111-118 (1989).
7. A. Gerhard, A. Bittner, "Second generation phosphate anti-corrosive pigments. Formulating rules for full replacement of new anti-corrosive pigments", *JCT*, **58** (740), 59-65 (1986).
8. Actirox - Hispafos. Non toxic and efficient anticorrosive pigments. Technical Specifications. Colores Hispania S.A.
9. M.H.L. Garnaud, "White corrosion inhibitive pigments", *Polymer Paint Colour Journal*, **18** (4), 268-270 (1984).
10. S.A. Hodges, W. Uphues, M.T. Tran, "1+2>3, Non toxic corrosion inhibitors synergisms", *Coatings World*, **2** (4) 32-35 (1997).
11. R. Romagnoli, V.F. Vetere, "Heterogeneous reaction between steel and zinc phosphate", *Corrosion (NACE)*, **51** (2), 116-123 (1995).
12. M. Cohen, "The breakdown and repair of inhibitive films in neutral solutions", *Corrosion (NACE)*, **32** (12); 461-465 (1976).
13. V. Anitha Kumari, K. Sreevalsan, S.M.A. Shibli, "Sodium molybdate for the effective protection of steel: a comprehensive review", *Corrosion Prevention & Control*, **48** (9), 83-96 and 109 (2001).
14. J.R. Ambrose, "The role of molybdenum as an inhibitor of localised corrosion on iron in chloride solutions", *Corrosion (NACE)*, **34** (1), 27-31 (1978).
15. R. Qvarfort, "Some observations regarding the influence of Molybdenum on the pitting corrosion resistance of stainless steel", *Corrosion Science*, **40** (2/3), 215-223 (1998).
16. C.A. Giúdice, J.C. Benítez, and V.J.D. Rascio: "Study of variables which affect dispersion of antifouling paints in ball mills", *JOCCA*, **63** (4), 153-158 (1980).
17. S. Gee, "Water-borne coatings", *Surface Coatings J.*, **80** (7), 316-22 (1997).



18. Z. Szklarska-Smialowska, R.W. Staehle: "Ellipsometric study of the formation of films on iron in orthophosphate solution", *J. Electrochem. Soc.*, **121** (11), 1393-1401 (1974).
19. M.C. Deyá, G. Blustein, R. Romagnoli, B. del Amo, "The influence of the anion type on the anticorrosive behaviour of inorganic phosphates", *Surface and Coatings Technology*, **150**, 133-142 (2002).
20. G. Blustein, B. del Amo, R. Romagnoli: "The influence of the solubility of zinc phosphate pigments on their anticorrosive behaviour", *Pigment & Resin Technology*, **29** (2), 100-107 (2000).

