

# THE PERFORMANCE OF ZINC MOLYBDENUM PHOSPHATE IN ANTICORROSIVE PAINTS BY ACCELERATED AND ELECTROCHEMICAL TESTS

*ESTUDIO DEL COMPORTAMIENTO DEL MOLIBDOFOSFATO DE CINC EN PINTURAS ANTICORROSIVAS POR MEDIO DE ENSAYOS ACELERADOS Y ELECTROQUIMICOS*

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## SUMMARY

*Red lead and zinc chromates are doubtless efficient pigments to protect metals against corrosion. Their use in paints formulation is being restricted due to their deleterious action. Zinc phosphate was firstly suggested to replace toxic chromates. However, data on their anticorrosive properties are not conclusive; so, a second generation of phosphate pigments, including zinc molybdenum phosphate, was developed.*

*In this paper, the anticorrosive behavior of micronized zinc molybdenum phosphate in paints with 30% of the pigment by volume and a PVC/CPVC ratio 0.8, formulated with different binders (alkyd, vinyl, chlorinated rubber and epoxy resins), was assessed by accelerated (salt spray cabinet and accelerated weathering) and electrochemical tests.*

*Epoxy and chlorinated rubber paints showed the best anticorrosive performance. The inhibitive action of zinc molybdenum phosphate was confirmed. Good correlation has been obtained between salt spray and electrochemical tests.*

**Keywords:** *ecological pigments; zinc molybdenum phosphate; alkyd, vinyl, chlorinated rubber and epoxy resins; anticorrosive paints; salt spray test; electrochemical assays.*

## INTRODUCTION

Organic coatings are an effective mean to protect steel against corrosive environments. Usually, anticorrosive paints contain lead or hexavalent chromium compounds; these pigments are particularly hazardous and contribute to contaminate the environment. Coatings today, and in the future, need to meet stringent environmental health and safety rules. Although heavy metal-containing primers have performed admirably in the past, today their use is not recommended. Zinc phosphate became one of the leading substitute for carcinogenic zinc chromate pigments [1-3].

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The protective action of zinc phosphate results from phosphatization of the metal substrate and the formation of complex substances with binder components [1,2]. More recent studies confirmed the presence of an oxyhydroxide film on the steel surface [4-6]. The protection mechanism would also imply the polarization of cathodic areas by the precipitation of sparingly soluble salts on the metal substrate [6-8]. The low solubility of zinc phosphate and the fact that this pigment is a coarse crystalline precipitate do not assist the growth of an effective anticorrosive film [3, 9-12].

Accelerated tests of zinc phosphate pigmented coatings led to disappointing results whereas outdoor long exposure tests showed the good performance of these paints [10, 13-22]. Present investigations point out that the protective properties of zinc chromate cannot be achieved by zinc phosphate [10, 13, 15, 23] except for alkyd paints [24]. As a consequence a second generation of modified zinc phosphate-based pigments was developed [10, 13-17].

Efforts to produce improved phosphate pigments were concentrated on the modification of the particle size and the pigment chemical composition. Smaller particle size results in optimum pigment packing. The chemical composition of the pigments was modified by adding molybdates, aluminium or by the use of surface organic pre-treatments.

Zinc molybdenum phosphate belongs to the so called second generation phosphate pigments; it is composed by zinc phosphate with zinc molybdate up to 1% (expressed as  $\text{MoO}_3$ ) and is claimed to have equal or higher anticorrosive behavior than chromates and undoubtedly better than zinc phosphate alone [25]. The pigment active inhibitive species is molybdate anion which repassivates corrosion pits in steel [26]. However, little information is available in the literature about its anticorrosive performance. Adrian and Bittner [3, 10, 13] reported the behavior of zinc molybdenum phosphate in alkyd paints in comparison with zinc phosphate and zinc chromate. The employment of zinc molybdenum phosphate and other pigments belonging to the second generation phosphate pigments series in compliant primers was also tested [13, 27].

The purpose of the present research is to study the anticorrosive properties of zinc molybdenum phosphate in solvent borne paints. Four binders were selected: alkyd, vinyl, chlorinated rubber and epoxy resins. Paints were formulated with a 30% pigment content by volume and a PVC/CPVC ratio 0.8. Their anticorrosive behavior was evaluated by accelerated and electrochemical tests. This paper continues previous research about zinc phosphate in paints formulated with different binders [24, 28].

## EXPERIMENTAL

### Paints composition and manufacture

**Binder.** The film forming materials were the followings: a medium oil alkyd (50 % linseed and tung oils, 30 % o-phthalic anhydride, 8 % pentaerythritol and glycerol and 12 % pentaerythritol resinate), vinyl resin (91 % vinyl chloride, 3 % vinyl acetate, 5.7 % alcohols)/tricresyl phosphate (4/1 ratio by volume) [29]; chlorinated rubber 10 cP/chlorinated paraffin 42 % (70/30 ratio by volume) and bisphenol A epoxy resin/polyamide (1/1 ratio by volume).

**Solvents.** The solvents employed were: white spirit for alkyd paints; cellosolve acetate/methyl isobutyl ketone/xylene (70/ 10/ 20, % by weight) for vinyl resin; xylene/Solvesso 100 (4/1 ratio by weight) for chlorinated rubber paints and toluene/methyl isobutyl ketone/butyl alcohol (36/52/12, % by weight) for epoxy paints.

**Pigment.** Micronized zinc molybdenum phosphate was employed as anticorrosive pigment, with two different contents, 15 and 30 % by volume with respect to the total pigment content. Titanium dioxide, talc and barium sulfate were also incorporated to the formulation to complete the pigment formula. The PVC/CPVC relationship was 0.8. The composition of the tested paints is shown in Table I.

**Table I**

**Solids in paint composition (% by volume)**

Paints	1	2	3	4	5	6	7	8
Zinc molybdenum phosphate	5.8	11.6	5.8	11.6	5.8	11.6	5.8	11.6
Titanium dioxide	5.6	4.8	5.6	4.8	5.6	4.8	5.6	4.8
Talc	13.8	11.3	13.8	11.3	13.8	11.3	13.8	11.3
Barium sulfate	13.8	11.3	13.8	11.3	13.8	11.3	13.8	11.3
Epoxy resin/polyamide resin (1/1 ratio)	61.0	61.0	--	--	--	--	--	--
Chlorinated rubber/chlorinated paraffin (70/30 ratio)	--	--	61.0	61.0	--	--	--	--
Vinyl resin/tricresyl phosphate (4/1 ratio)	--	--	--	--	61.0	61.0	--	--
Medium oil alkyd	--	--	--	--	--	--	61.0	61.0

**NOTE:** The solvent mixture employed for epoxy paints was toluene/ methyl isobutyl ketone/ butyl alcohol (36/52/12, % by weight); for chlorinated rubber paints was xylene/Solvesso 100 (4/1 ratio by weight); for vinyl resin was cellosolve acetate/methyl isobutyl ketone/xylene (70/10/20, % by weight) while white spirit was used for alkyd paints.

**Paints manufacture and application.** Paint manufacture was carried out employing a ball mill with a 3.3 liters jar. The pigments were dispersed in the vehicle for 24 hours to achieve an acceptable dispersion degree [30].

The paints were applied by means of a spray gun on SAE 1010 steel panels (15.0x7.5x0.2 cm) up to a thickness of  $75 \pm 5 \mu\text{m}$ . SAE 1010 steel composition is as follows: C: 0.12%, Si: 0.01%, Mn: 0.35%, S: 0.02%, P: 0.02%. Tested panels were previously sandblasted to Sa 2 1/2 (SIS 05 59 00) attaining  $20 \pm 4 \mu\text{m}$  maximum roughness and degreased with toluene. A second series of panels was prepared by topcoating primed specimens with a dry film thickness of  $40 \pm 5 \mu\text{m}$ . The painted panels were kept in the laboratory for 7 days before testing.

## Laboratory tests

**Salt spray test (ASTM B 117).** A scratch line was made through the coating with a sharp instrument so as to expose the underlying metal to the aggressive environment. After 650 and 1300 hours exposure, the panels were evaluated to establish the rusting degree (ASTM D 610) and to assess failure at the scribe (ASTM D 1654). In all cases experiences were carried out in triplicate, determining the mean value of the results obtained.

**Accelerated weathering (ASTM G 26).** The accelerated degradation of painted samples was carried out in an Atlas Weather-Ometer (Xenon arc type). The test program consisted of a 102 minutes light cycle followed by a 18 minutes light and water spray cycle. The overall time of each cycle was 2 hours and that of the complete test 720 hours. Test specimens were observed and evaluated for blister formation, degree of rusting and failure at the scribe marks, according to the above mentioned standard specification.

**Corrosion potential measurements.** The electrochemical cells were constructed by delimiting 3 cm<sup>2</sup> circular zones on the painted surface. An acrylic tube, with one flat end and 7 cm high, was then placed on the specimen and filled with the electrolyte (0.5 M sodium perchlorate solution). The measurements of the corrosion potential of the coated steel were made using a calomel electrode as reference and a high impedance voltmeter.

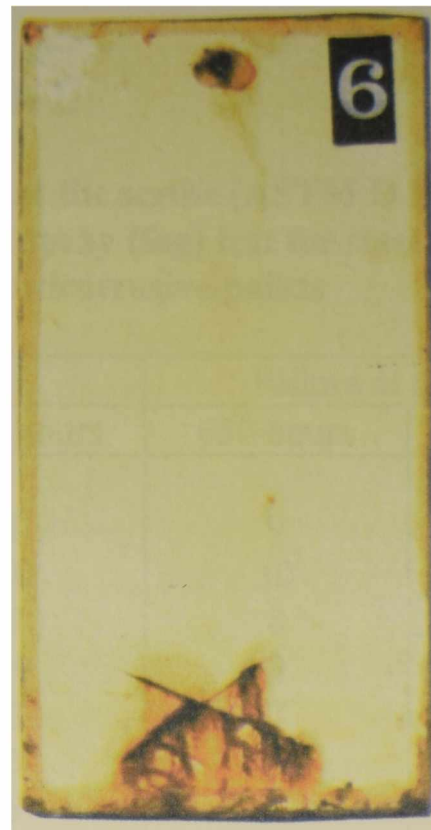
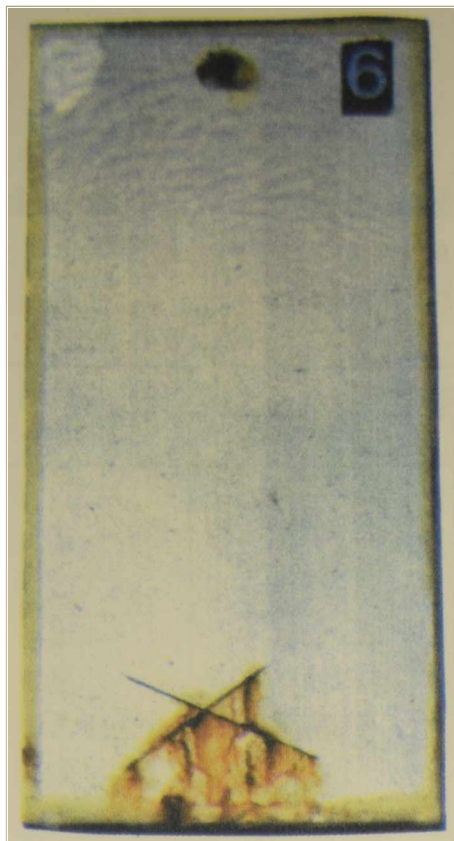
**Resistance measurements.** The resistance between the steel substrate and a platinum electrode was also measured employing the cells described previously and an ATI Orion, model 170 conductivity meter which operates at a 1000 Hz frequency. Similar measurements were performed on uncoated steel.

**Polarization resistance measurements.** The polarization resistance of painted specimens was determined as a function of immersion time employing an electrochemical cell with three electrodes. The reference electrode was a calomel one and the counterelectrode a platinum grid. The voltage swept was  $\pm 10$  mV, starting from the corrosion potential. Measurements were done employing an EG&G PAR Potentiostat/Galvanostat, Model 273A and the software SOFTCORR 352. Polarization resistance of uncoated steel was also monitored as a function of the immersion time.

## RESULTS AND DISCUSSION

**Salt spray test (ASTM B 117).** The results obtained in the salt spray cabinet after 650 and 1300 hours of testing are shown in Tables II and III. None of the paints showed blistering during this test. The anticorrosive protection achieved with the epoxy resin was the most efficient for both pigment contents (Fig. 1 and 2). A similar behavior was observed for paints formulated with chlorinated rubber.

Topcoating of panels improved notably the anticorrosive behavior in such a way that all paint systems showed a good performance in this test after 1300 hours exposure (Fig. 3) and no corrosion spots were observed in the intercoat zone. After removing the anticorrosive paint only a slight uniform non aggressive corrosion products film was detected in the case of panels coated with vinyl and alkyd paints pigmented with 15% of zinc molybdenum



**Fig.1.- Panels covered with the epoxy paint (30% zinc molybdenum phosphate) exposed for 650 (left) and 1300 (right) hours to the salt spray cabinet (ASTM B 117).**



**Fig.2.- Panel covered with the epoxy paint (15% zinc molybdenum phosphate) exposed for 1300 hours to the salt spray cabinet (ASTM B 117).**



**Fig. 3.- Panels covered with the vinyl paint (15% zinc molybdenum phosphate) and a topcoating, exposed during 1300 hours to the salt spray cabinet (ASTM B 117).**



phosphate. Obviously, the improved behavior was due to the increased barrier effect obtained by topcoating the primed panels.

**Table II**

**Rusting degree (ASTM D 610) and failure at the scribe (ASTM D 1654) after 650 and 1300 hours exposure in the salt spray (fog) test for steel panels covered with the anticorrosive paints**

Paint	Rusting		Failure at the scribe	
	650 hours	1300 hours	650 hours	1300 hours
1	8	8	9	9
2	10	10	10	10
3	9	9	8	7
4	10	10	9	8
5	8	7	7	6
6	6	5	6	5
7	6	5	6	5
8	7	6	8	7

**Table III**

**Rusting degree (ASTM D 610) and failure at the scribe (ASTM D 1654) after 650 and 1300 hours exposure in the salt spray (fog) test for steel panels covered with the anticorrosive paint plus a topcoat**

Paint	Rusting		Failure at the scribe	
	650 hours	1300 hours	650 hours	1300 hours
1	10	10	10	10
2	10	10	10	10
3	9	9	9	9
4	10	10	10	10
5	9	8	9	7
6	10	10	8	8
7	8	6	7	6
8	9	7	6	5

In this test, the anticorrosive behavior of epoxy and chlorinated rubber paints pigmented with zinc molybdenum phosphate was notably improved with respect to similar paints formulated with zinc phosphate; to achieve a similar performance the latter paints needed a topcoat (40  $\mu\text{m}$  thickness). In the case of chlorinated rubber, in spite of being topcoated, 0.03% of the metallic surface showed signs of corrosion [31].

Vinyl paints containing zinc molybdenum phosphate showed an extended life with respect to those containing zinc phosphate. Both types of paints obtained the same qualification but the former after a 650 exposure period and the latter after 400 hours [32]. A similar feature was noticed with the alkyd binder [31].

If comparison is made with respect to paints formulated with zinc chromate and the less resistant resins (vinyl and alkyd), it must be pointed out that paints with vinyl resin failed in this test after 96 hours exposure developing pits on the painted surface [32] and substitution by zinc molybdenum phosphate resulted clearly advantageous. Non significant differences in the anticorrosive performance were observed between alkyd paints pigmented either with zinc chromate or with zinc molybdenum phosphate [24].

Undercutting rusting was similar for paints containing zinc phosphate and for paints pigmented with zinc molybdenum phosphate; however results obtained with phosphate pigments and alkyd binder are notably improved with respect to zinc chromate [24, 32].

**Accelerated Weathering (ASTM G 26).** All paints exhibited a good behavior after 720 hours exposure. No blister or significant signs of corrosion were observed on the surface of the painted panel. Again, topcoating of panels covered with anticorrosive paints enhanced barrier properties of the system improving the behavior of vinyl and alkyd systems (Table IV). It may be expected that these paint systems would perform acceptably in outdoor exposures for at least two years without showing signs of corrosion because 700 hours of accelerated weathering are approximately equivalent to 2 years outdoor exposure [33].

**Table IV**

**Rusting degree (ASTM D 610) and failure at the scribe (ASTM D 1654) after 360 and 720 hours exposure in the Weather-Ometer for steel panels covered with the anticorrosive paints plus a topcoat**

Paint	Rusting		Failure at the scribe	
	360 hours	720 hours	360 hours	720 hours
1	10	10	10	10
2	10	10	10	10
3	10	10	10	10
4	10	10	10	10
5	10	9	10	9
6	10	10	10	10
7	10	8	10	8
8	10	9	10	9

NOTE: None of the samples presented blistering.

**Corrosion potential measurements (Fig. 4).** The corrosion potential of panels coated with paints formulated with chlorinated rubber and epoxy resins shifted towards more positive values as time elapsed to finally decay slightly after 25 and 50 days of immersion, respectively.

For chlorinated rubber paints, the corrosion potential rised again after 40 days of immersion due to the sealing of the small pores of the paint film by corrosion products as it was observed by a visual inspection. Pigment-binder interaction could also be responsible for the shifting of the corrosion potential during the test period in epoxy paints; but this requires a deeper study. Accordingly, both paints showed the best anticorrosive performance in the salt spray test, so corrosion potential measurements support the results obtained in this test.

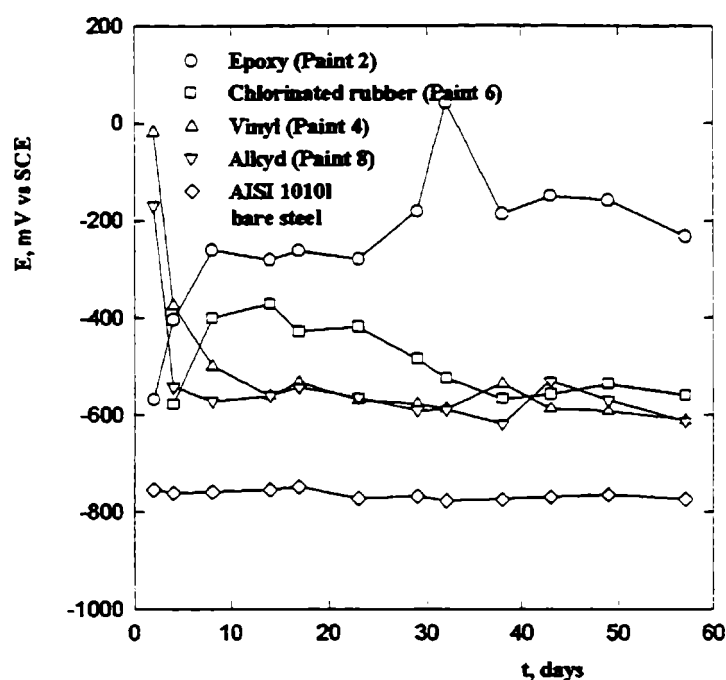


Fig. 4.- Corrosion potential of painted steel panels as a function of the exposure time in 0.5 M sodium perchlorate solution.

The corrosion potential of panels covered with paints formulated with alkyd and vinyl resins shifted towards more positive values with respect to the corrosion potential of bare steel in 0.5 M sodium perchlorate solution during the first 24 hours of immersion. After one day, the corrosion potential derived quickly towards more negative values because of the increasing number of conductive paths through the paint film and the concomitant incoming of the electrolyte solution (Fig.5); after a few days these paints attained the final value which was displaced, at least, +150 mV with respect to the corrosion potential of bare steel.

The corrosion potential of painted steel changed as the corroded area increased but it never matched the corrosion potential of bare steel because a fractional area of the test specimen remained undamaged, free from blisters and corrosion spots (99 % for chlorinated rubber paint, 100 % for epoxy, 94 % for vinyl and 40 % for alkyd paints) at the end of the test part of the attacked area is passivated as it would be seen later.

In every case, the shifting of the corrosion potential to more noble values is due to the low film permeability and to the presence of zinc molybdate in the paint film [34, 35]. Mo(VI) compounds constitute the passive layer together with phosphates [36]. Ambrose [26] found that molybdenum compounds are effective in increasing the repassivation rate in crevices and pits.

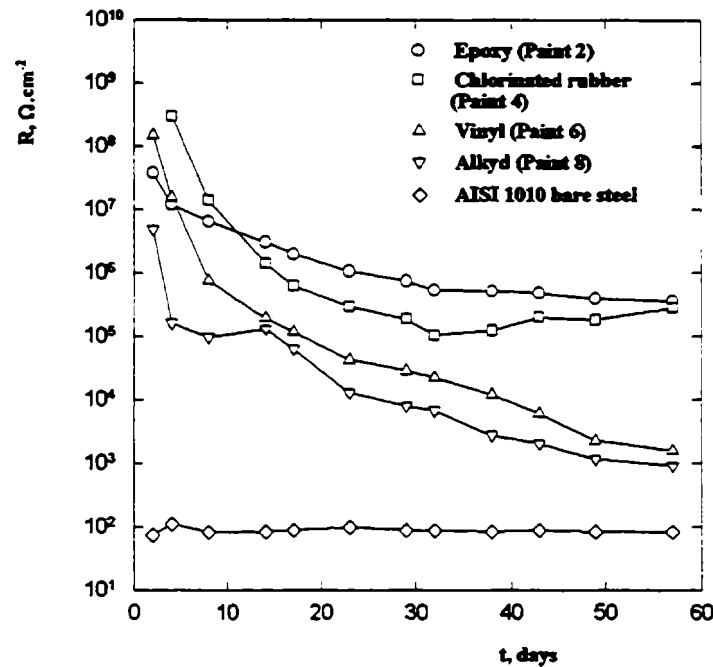


Fig. 5.- Resistance of painted steel as a function of the exposure time in 0.5 M sodium perchlorate solution.

A diminishing of the zinc molybdenum phosphate content to 15 % impaired the anticorrosive protection since the corrosion potential shifted towards more negative values with the immersion time; however, epoxy paints still showed good anticorrosive performance. No significant changes were detected among panels covered with paints formulated with alkyd and vinyl resins which, anyway, rapidly acquired the final corrosion potential. For the sake of simplicity, only paints formulated with a 30 % of the pigment were plotted.

**Resistance measurements** (Fig. 5). The measured resistance is composed of two contributions: the solution resistance and the paint film resistance. As the solution resistance is low (84  $\Omega$ ) the paint film resistance is responsible of the measured values. Polarization effects may be neglected at the measuring frequency employed in this test. The initial values for the ionic resistance decreased as follows:

$$R_{\text{paint 3 and 4}} > R_{\text{paint 6}} > R_{\text{paint 5}} > R_{\text{paint 2}} > R_{\text{paint 7 and 8}} > R_{\text{paint 1}}$$

and the final values decreased according to:

$$R_{\text{paint 3 and 4}} = R_{\text{paint 2}} > R_{\text{paint 1}} > R_{\text{paint 6}} = R_{\text{paint 5}} > R_{\text{paint 7 and 8}}$$

The initial values of the ionic resistance are of crucial importance because they are employed to predict the useful life of the coating. All paints originated films with an initial ionic resistance high enough ( $>10^6 \Omega \cdot \text{cm}^2$ ) to protect steel by a barrier effect, however, full protection is achieved when the ionic resistance exceeds  $10^8 \Omega \cdot \text{cm}^2$  [37, 38]. In this sense, vinyl and chlorinated rubber paints exhibited the highest initial barrier effect. However, as time went on, chlorinated rubber and epoxy coatings proved to be the most resistant ones to water

and ion penetration and this fact ensured an excellent performance of both paints during the immersion period.

Although chlorinated rubber paint showed the highest ionic resistance values at the beginning of the test, it also denoted a higher tendency to produce pinholes with respect to epoxy paints. Pore sealing by corrosion products in chlorinated rubber paints, after 32 days of immersion, is noticed by the slight increment of the ionic resistance at the end of the immersion period. Epoxy paints did not show spots of iron oxides neither on the paint film nor under it during the test period, the ionic resistance decreased slowly as time elapsed.

Vinyl and alkyd paints showed abrupt changes in the ionic resistance during the first days of immersion resulting in an increasing permeability to the electrolyte solution through macropores which reach the base metal. It was demonstrated that the electrolyte located inside the polymer net does not affect the conduction through coating [39]. When the ionic resistance fell in the  $10^4$ - $10^5$  range, the corrosion potential reached its final average value and it coincided with total electrolyte penetration through the coating and, eventually, blister formation, as stated by Szauer [38].

When the pigment content was lowered from 30 to 15% the initial ionic resistance decreased, as an average, by two orders of magnitude; this means that in the case of vinyl and alkyd paints the initial barrier effect is lost and in the other cases diminished.

**Polarization resistance measurements** (Fig. 6). Polarization resistance, as measured in this research, is not a true one because it includes the ionic resistance. However, in all cases it is higher than the ionic resistance, this fact reveals that the tested pigment has inhibitive properties [38] which is in agreement with previous results where zinc phosphate (the main component of the so called zinc molybdenum phosphate) reduced the corrosion rate of iron [6]. The inhibitive action of the pigment is due to the precipitation of a ferric phosphate layer on the metal surface. Phosphate adheres partially to the metal surface and loose ferric phosphate plugging paint film pores. Ferrous phosphate may be formed as a previous stage and iron oxides precipitated on the metal surface too [40]. Visual inspection of exposed panel showed that ferric oxide spots were partially converted in more stable ferric phosphate. It was demonstrated that molybdenum compounds increase the polarization resistance of steel and improved the corrosion resistant of the substrate still in the presence of chlorides [34]. The addition of molybdenum hexavalent anions decreases the critical current density for passivation and increases the stability of passive films. The presence of silicon in the steel employed in this research may contribute to enhance the effect of molybdenum [41].

Panels painted with chlorinated rubber and epoxy paints showed the highest polarization resistance values and vinyl and alkyd paints showed an important decrease of this magnitude with the immersion time. As a general rule, changes in polarization resistance are correlated with changes in the ionic resistance.

Alkyd paints polarization resistance may be ten times higher than the electrolyte resistance ( $84\ \Omega$ ) and this may be attributed not only to the inhibitive action of the pigment but also to the high reactivity of this pigment with the alkyd resin; the inhibition of corrosion of steel by soap formation was known from early times [1, 2, 42, 43]. As a consequence, it presented less ferric oxide spots than it could be expected from the low electrolyte resistance

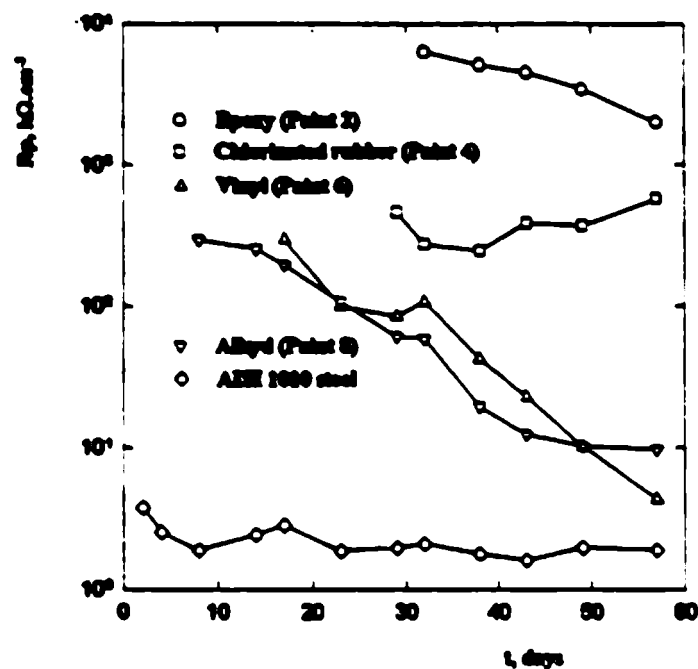


Fig. 6.- Polarization resistance of painted steel panels as a function of the exposure time in 0.5 M sodium perchlorate solution.

values registered during the test. However, it formed some blisters; under which the metal surface remained free from oxides.

Visual examination of painted panels revealed that ferric oxide spots were partially converted into non adherent non expansible ferric phosphate by the action of the pigment.

## CONCLUSIONS

1. Paints formulated with epoxy and chlorinated rubber resins still showed a good anticorrosive performance with a zinc molybdenum phosphate content as low as 15% by volume with respect to the total amount of pigments. However, a 30% content is recommendable to obtain the best performance of each type of binder.
2. The higher values of the polarization resistance with respect to the ionic one show that zinc molybdenum phosphate has inhibitive properties against corrosion.
3. In general, due to the efficiency of the total scheme applied on steel, all samples showed a good behavior in the Weather-Ometer test after 720 hours of exposition.
4. Good correlation was found between salt spray test and electrochemical tests. A relationship was noticed among corrosion potential, ionic resistance and polarization resistance but this aspect deserves a further research.

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