A new pigment for smart anticorrosive coatings

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Abstract The purpose of this paper was to evaluate the performance of a modified zeolite as an anticorrosive pigment for paints. A procedure to prepare the pigment was outlined and its anticorrosive properties assessed following the electrochemical behavior of a steel electrode in pigment suspension. In a second stage, alkyd paints were formulated employing different anticorrosive pigments: (1) 30% by volume (v/v) of the modified zeolitic rock, (2) 10% (v/v) of zinc phosphate, and (3) a mixture of 10% (v/v) zinc phosphate plus 20% (v/v) of the modified zeolitic rock. In every case, percentages were referred to the total pigment content. Titanium dioxide, zinc oxide, and barium sulfate were incorporated to complete the pigment formula. The pigment volume concentration/critical pigment volume concentration (PVC/CPVC) ratio was 0.8. The performance of the resulting anticorrosive paints was assessed by accelerated (salt spray and humidity chambers) tests and electrochemical (corrosion potential, ionic resistance, and polarization resistance) essays. It was demonstrated that the modified zeolite is effective in protecting steel from corrosion when it is used in combination with zinc phosphate. There exists a synergism between the modified zeolite and zinc phosphate that allows the zinc phosphate content in anticorrosive paints to be reduced.

Keywords Zeolite, Molybdenyl cation, Anticorrosive pigment, Alkyd paints, Accelerated tests, Electrochemical essays

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Introduction

From 1970 to the present, two major goals have been achieved in the field of paint technology: the replacement of toxic inhibitive pigments and the progressive elimination of solvents in paint formulations to fit VOC regulations. Traditional anticorrosive paints contained lead or hexavalent chromium compounds as active pigments. These pigments contaminated the environment and, at the same time, represented a risk to human health. Many compounds have been suggested as possible replacements for chromates and lead compounds but zinc phosphate[1–10] and related substances became the leading substitutes for toxic inhibitors.[7–25] Other strategies have been developed to improve the performance of zinc phosphate. One of them consisted of the employment of more effective complementary pigments, such as zinc oxide or silicates, which reduced the level of the anticorrosive pigment content. Natural silicates (wollastonite, mica, etc.) have been employed for many years in anticorrosive paints. More recently, they have begun to find increasing acceptance for use after a suitable surface treatment.[26,27]

Due to the imposition of increased legislative restrictions on the emission of organic materials into the atmosphere, waterborne coatings are becoming more and more important for both do-it-yourself and industrial coatings applications. Water, as a solvent, has two main advantages because it is nontoxic and nonflammable. Waterborne systems present a range of characteristic differences and, in some cases, difficulties not exhibited by solvent borne paints.[28–32] It has been stated that waterborne paints are less resistant to the corrosion process generated by water, ions, and oxygen permeation and more prone to biological attack.[29,33–36] If no specific inhibitors are added to the formulation, they may also exhibit "flash rusting" during solvent evaporation, which finally affects the appearance of the coating.[33,36,37]

More recently, the challenge in the field of paint technology has been to formulate smart coating which are structured coating systems that provide an optimum selective response to an external stimulus such as temperature, stress, strain, corrosion, and so on. Their smart behavior results from scientific combinations of intrinsic coating properties and the incorporation of nanotechnologies. Ideally, a smart corrosion-inhibitive coating will generate or release an inhibitor only when demanded by the initiation of corrosion. In this sense, different types of smart coatings were proposed in the literature: paints formulated with conducting polymers, self-healing coatings, coatings with ion-exchanging pigments, and more.[38–40]

Zeolites constitute a versatile material that has found many technological applications. The employment in paint technology is rather restricted, but zeolites have been used as humidity- and ammonia-adsorbent material in ceiling paints[41] and finishing paints.[42] In this last application, zeolites were exchanged with suitable cations, heated at 350°C, and then mixed with mineral silicate ligands to obtain paints for different substrates with acceptable hiding power. Zeolites exchanged with silver ions were employed in smart hygienic coatings as biocides, due to the ability of silver ions to inhibit vital processes in microorganisms.[43] Because zeolites are ionic-exchanging materials, it seemed reasonable to prepare anti-corrosive pigment by exchanging sodium cations in zeolites with other cations that have inhibiting properties. For example, molybdenum cations could be exchanged by the zeolite. It was thought that these ions, back-exchanged to the environment, could generate inhibitive species such as molybdates.

The objective of this research was to develop a modified zeolite to replace phosphate pigments in anticorrosive paints. The modified zeolite was prepared by ionic exchange with molybdenyl ions. The anticorrosive properties of this exchanged zeolite were studied using electrochemical techniques, employing a dispersion of the inhibitor in the adequate supporting electrolyte and formulating anticorrosive coatings. Coatings performance was evaluated by accelerated (humidity chamber and salt spray test) and electrochemical (corrosion potential, ionic resistance, and polarization resistance) tests.

Experiment

Obtention and characterization of the pigments

The zeolitic rock employed in this research was obtained from an Argentine mine, located in the San Juan Province, and ground to obtain a particle whose average diameter was equal to 400 nm (see Table 1). Particle size distribution was obtained with a Micromeritics SediGraph analyzer that uses the Stokes' law to measure particle size distribution of finely powdered

Table 1: Particle size distribution

Equivalent spherical diameter (μm)	Cumulative mass percentage
0.4	93.5
1.0	95.0
2.0	96.0
4.0	96.5
10.0	98.5
15.0	99.0
20.0	100.0

materials when dispersed in a liquid (the measurement range was 100–0.1 μm). The instrument uses a finely collimated beam of low energy X-rays to measure the concentration of particles at different depths. Results are given as accumulated mass percentages as a function of the equivalent spherical diameter. The ground zeolitic rock was heated at 350°C to eliminate water, thus activating the zeolite particle and improving physical properties such as its exchanging capacity.[44,45] The capacity of the zeolite for ionic exchange was measured using an ammonium salt solution, as suggested in the literature.[46] It was found to be equal to ~105 milliequivalents of cation per 100 g of zeolite, and changed to ~120 milliequivalents when heated at 350°C. The ground zeolitic rock was modified by ionic exchange in a beaker, bringing it in contact with a molybdenyl cation solution during a 24-h period, with continuous stirring. The modified zeolite was finally filtered and washed several times with distilled water (one time with a 1% sodium acid carbonate solution and distilled water) until the neutrality of the filtrate was achieved. The final product was dried at room temperature until constant weight was achieved. The molybdenyle solution was prepared by dissolving 10 g of molybdic acid in 90 mL of 1 M sulfuric acid, plus 10 mL of concentrated sulfuric acid, and heating the system to achieve complete dissolution.

A good quality zinc phosphate, PZ 20, was selected to be used in this research; it was purchased from the Societé Nouvelle des Couleurs Zinciques.[47] Its composition was controlled by dosing the phosphate and the zinc contents by means of conventional analytical procedures and its anticorrosive behavior was checked in previous research.[48]

The UV–vis reflectance spectra of pigments were recorded to obtain their characteristic peaks for further identification in surface analyses of exposed steel panels.

Evaluation of the properties of inhibitive pigment

Because the anticorrosive pigments tested in this research (modified zeolite, zinc phosphate, and modified zeolite/zinc phosphate, 2/1 by volume) were insoluble substances, their inhibitive properties were assessed employing a dispersion of the pigment in a

supporting electrolyte and stirring the dispersion to avoid pigment settlement. This, in turn, may have generated premature corrosion of the steel substrate. The corrosion potential of an SAE 1010 steel electrode was measured in a dispersion of the pigment in 0.025 M $NaClO_4$ during a 24 h period. The saturated calomel electrode (SCE) was used as a reference.

The morphology of the protective layer, generated on the steel surface by exposition to the dispersion of the anticorrosive pigments in 0.025 M $NaClO_4$ during a 24-h period, was studied by scanning electron microscopy (SEM) and the surface composition by energy dispersive analysis of X-ray (EDXS) and UV–vis diffuse reflectance spectroscopy. The reflectance spectra were recorded with a GBC CINTRA 40/UV-Visible Spectrometer. Spectra were scanned in the 200–800 nm range at 50 nm per min.

Anodic and cathodic polarization curves of a steel electrode (working electrode), in contact with the pigment dispersed in 0.5 M $NaClO_4$, were obtained after 6 h of exposure. An SCE was used as reference and a platinum grid was used as the counterelectrode. The swept began in the vicinity of corrosion potential, at a scan rate of 1 mV s^{-1}.

Composition, manufacture and application of paints

The resin used to formulate the paint films to carry out this research was a medium oil alkyd (50% linseed oils, 30% *o*-phthalic anhydride, 8% pentaerythritol and glycerol, and 12% pentaerythritol resinate). The resin, whose trademark is ALKIPOL 352/50, was provided by POLIDUR S.A. of Argentina.

The paints contained different anticorrosive pigments. Paint Z1 had 30% (v/v) of the modified zeolite, Paint Z2 had 10% zinc phosphate, and Paint Z3 contained 10% of zinc phosphate plus 20% of the modified zeolite. All pigment contents were referred to the total pigment content. In the case of Paints Z1 and Z3, the anticorrosive pigment loading was 30%, which is the percentage recommended in the literature for achieving good results with phosphate pigments.[9–12] The lower percentage for Paint Z2 was chosen on purpose because poor behavior was previously observed with low percentages of this pigment.[49] In the case of Paint Z3, the total pigment content was adequate but two-thirds of the anticorrosive pigment was replaced by the modified zeolite to see how they influence each other.

Titanium dioxide, zinc oxide, and barium sulfate were incorporated to complete the pigment formula. The pigment volume concentration/critical pigment volume concentration (PVC/CPVC) relationship was 0.8. The CPVC value was determined by the oil absorption method according to ASTM D 1483 and the PVC/CPVC ratio was that recommended in current literature for phosphate pigments.[9–12] The PVC value was easily obtained from CPVC and the selected value

Table 2: Paint composition (% by volume)

Paints	Z1	Z2	Z3
Zinc phosphate	–	2.2	1.6
Modified zeolite	5.9	–	3.2
Titanium dioxide	2.3	4.3	1.9
Barium sulfate	5.7	8.0	4.6
Zinc oxide	5.7	8.0	4.6
Alkyd resin (1:1)	51.7	49.8	54.1
White spirit	28.7	27.7	30.0

for the PVC/CPVC ratio. The composition of the different paints is shown in Table 2.

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

Laboratory tests

A set of three panels were put in the salt spray chamber (ASTM B 117) to evaluate the degree of rusting (ASTM D 610) and blistering (ASTM D 714). The examination of the painted panels was done after 340, 840, 1500, and 2300 h of exposure. In all cases, tests were carried out in triplicate, determining the mean value of the obtained results. The adhesion of the coatings to the steel substrate was measured by the tape pull test (ASTM D 3359) after 340 and 840 h exposure; results were compared with the values that were obtained before placing the panels into the salt spray chamber.

After the panels were taken out of the salt spray chamber, the paint films were removed by employing suitable organic solvents. Xylene was used to soften the film, and THF was used to finally remove it. Uncoated panels were observed by SEM and EDAX. In addition, the UV–vis diffuse reflectance spectra of the panels' surface were obtained. Another set of panels was placed in the humidity chamber (ASTM D 2247) and evaluated after 500 and 840 h to establish the degree of blistering and the rusting.

The electrochemical cells used to measure the corrosion potential were constructed by delimiting 3 cm^2 circular zones on the painted surface. An acrylic tube was placed on the specimen and filled with the electrolyte (0.5 M sodium perchlorate solution). The corrosion potential of coated steel was measured by employing an ECS as reference and a high impedance voltmeter. The resistance between the coated steel substrate and a platinum electrode was also measured by employing the cells described above and an ATI Orion (Model 170) conductivity meter at 1000 Hz.

The polarization resistance of painted specimens was also determined as a function of immersion time, by employing the cell described previously but with a platinum counterelectrode. The reference electrode

was the ECS and the counterelectrode was a platinum grid. The voltage scan was ±10 mV, starting from the corrosion potential at a scan rate of 0.166 mV per s. A small amplitude scan was chosen to minimize the loss of coating adhesion to the substrate by polarization. Measurements were done by employing a Model 273A EG & G PAR Potentiostat/Galvanostat plus SOFT-CORR 352 software.

Results and discussion

Molybdenyl cation is of a complex nature and is formed in strong mineral acid solutions, particularly sulfuric acid.[50] The chemical equation for interpreting molybdenyl formation and the ionic-exchange reaction with the zeolite (Z), respectively, may be written as follows:

$$MoO_4^{2-} + 4\ H^{1+} \leftrightarrow MoO_2^{2+} + 2\ H_2O$$

$$2Na/2Z + MoO_2^{2+} \leftrightarrow MoO_2^{2+}/2Z + 2Na^{1+}$$
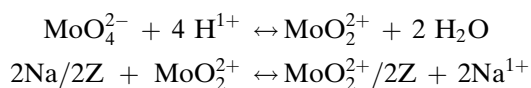
The amount of molybdenum exchanged by the zeolite was ~4.4 milliequivalents of cation per 100 g of the ground zeolitic rock. This was lower than in the case of ammonium or sodium ions. However, 0.32% of molybdenum was encountered in the analysis of the solid and, most importantly, molybdenum may be brought back into solution under appropriate conditions; for instance, in the presence of sodium ions. The amount of molybdenum in the solid did not change significantly with the particle size of the modified zeolite. This led to the conclusion that molybdenyl cation was exchanged by the zeolite and not adsorbed onto the zeolite particle surface. In addition, zeolites must be conditioned by employing cationic surfactants for anion sorption.[51]

The preceding chemical equations give the basis for understanding the smart behavior of the modified zeolite. When water and ions (sodium ions, for instance) penetrate the coating, these ions are exchanged for molybdenyl cations. These cations readily hydrolize to generate molybdate anions. The chemical equations used to interpret this behavior are just the inverse of those written previously. Molybdates are known to passivate a steel substrate by forming a ferrous molybdate layer.

The UV–vis spectrum of the modified zeolitic rock show three peaks: one at 212 nm, another at 265 nm, and a third at 318 nm. They are normally attributed to charge transfer processes between iron ions in different oxidation states. Iron oxides are found in zeolites and, if necessary, could be eliminated by suitable acid treatment.

Results of the electrochemical tests to evaluate the inhibitive properties of pigments

The corrosion potential of the steel panel in contact with the modified zeolite was –647.5 mV after 24 h of immersion in 0.025 M NaClO$_4$. The protective layer appeared to be a cracked film with small spherical formations embedded in it. The spheres contained high amounts of molybdenum (92.26% of MoO$_3$), and very low amounts of iron (7.74% of Fe$_2$O$_3$). The gel-like formation was also rich in molybdenum. These findings confirmed that the exchanged zeolitic rock really acted as a smart pigment because the molybdenum species, which initially were retained in the zeolite, now appeared on the metallic surface. It was reported in the literature that molybdenum formed a film on the steel surface that restrained corrosion, although this film was seldom observed.[52,53] In this experiment, it could be clearly appreciated and confirmed that the protective layer is a molybdate film that dissolved as corrosion continued over time (see Fig. 1).

The corrosion potential of the steel panel with zinc phosphate after immersion in 0.025 M NaClO$_4$ was –503.4 mV, but no corrosion signs appeared on the surface that were visible to the naked eye. The protective layer, observed by SEM, was a uniform oxide film that may eventually contain zinc oxide.[54]

The corrosion potential of the steel panel with the modified zeolite and zinc phosphate was found to be –679.6 mV. As in the case of steel in contact with zinc phosphate, no corrosion signs were detected on the metallic surface. The morphology of the protective layer was more complicated than in the previous cases. The first layer was composed of a more or less uniform film on which big crystals and plates grew. The bare layer was primarily composed of iron oxide. The make up of the crystals and plates was rather complex and similar in nature. The main components were P$_2$O$_5$ (26.37%) and ZnO (53.75%), with smaller amounts of FeO (17.53%) and MoO$_3$ (2.35%) (see Fig. 2). It seemed that molybdenum allowed a better phosphating of the bare metal.
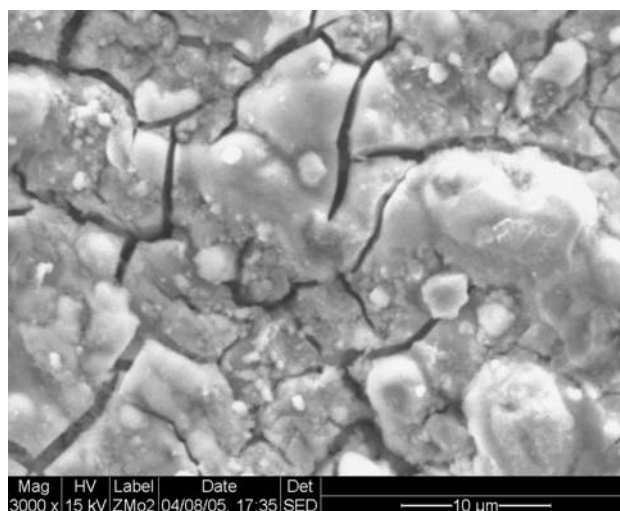

Fig. 1: SEM micrograph of film formed on the steel panel in contact with modified zeolitic rock aqueous suspension (3000x)
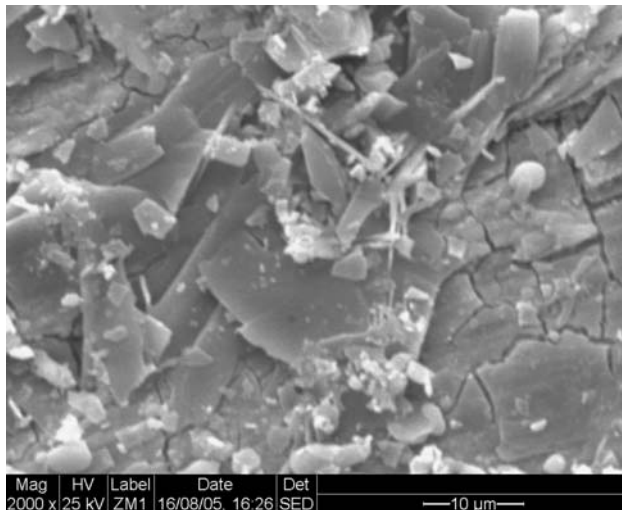
Fig. 2: SEM micrograph of film formed on the steel panel in contact with modified zeolitic rock–zinc phosphate aqueous suspension (2000x)

Fig. 4: Cathodic polarization curves of steel in contact with pigment suspensions

In all cases, the deconvolution of the UV–vis spectra of steel, in contact with pigments dispersed in the supporting electrolyte, showed the presence of α-FeOOH (peaks at 406 and 648 nm) and α-Fe$_2$O$_3$ (peaks at 500 and 360 nm).[55–57] The presence of zeolite particles on the panels in contact with the suspension of the modified zeolitic rock, or the modified zeolite and zinc phosphate, was detected through the characteristics peaks of zeolites.

The anodic polarization curves of the inhibitive pigments' dispersion is shown in Fig. 3. At low overpotentials, the curve describing steel dissolution in zinc phosphate suspension had lower currents than those obtained with the exchanged zeolite, indicating that
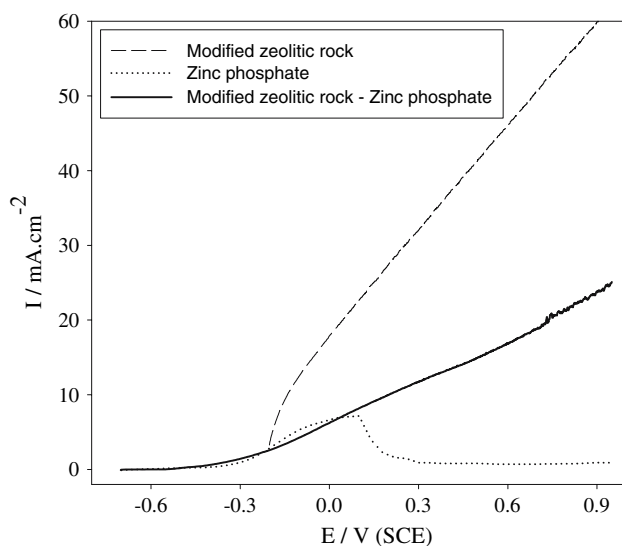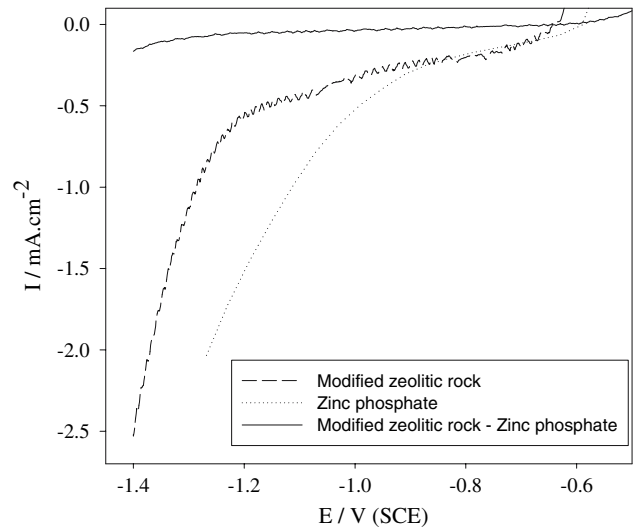
zinc phosphate appeared to be more efficient in restraining steel dissolution. The dissolution of the steel electrode in the suspension containing zinc phosphate and modified zeolite appeared to be quite inhibited in a wide potential interval. Cathodic polarization curves (see Fig. 4) obtained with the modified zeolite did not show evidence of corrosion inhibition. In phosphate suspension, the cathodic current was diminished but the lowest values were observed on the suspension containing the modified zeolite and zinc phosphate.

Results of the accelerated tests

Results obtained in the salt spray chamber are shown in Table 3. Paint Z1, pigmented with the modified zeolite, showed disappointing behavior because it could not surpass 340 h of exposure. Corrosion spots and blisters appeared during the second week of essay. The degradation of the paint containing zinc phosphate (Paint Z2) could be clearly appreciated after 840 h, while the paint with zinc phosphate and the modified zeolite (Paint Z3) showed, at that moment, very little rusting and no blisters. The panels coated with this paint underwent 1500 h of exposition with a good qualification (rusting degree of 8) that dropped to 7 after 2300 h.

Once the coating was removed, the surfaces of the panels were analyzed by UV–vis diffuse reflectance spectroscopy to identify any corrosion products on them. The presence of α-Fe$_2$O$_3$ was detected, as was the presence of zeolite particles in the case of panels coated with Paints Z1 and Z3, as revealed by the characteristic peaks of the modified zeolite.

The most important conclusion derived from this experiment is that the anticorrosive behavior of paints

Fig. 3: Anodic polarization curves of steel in contact with pigment suspensions

Table 3: Adhesion of the coatings to the substrate and degree of paint rusting and blistering in the salt spray chamber

Paint	Hours								
	0	340			840			1500	
	Adhesion	Adhesion	Rusting	Blistering	Adhesion	Rusting	Blistering	Rusting	Blistering
Z1	5B	0B	6	4 MD	–	–	–	–	–
Z2	5B	5B	8	10	0B	6	6D	–	–
Z3	5B	5B	10	10	5B	9	10	8	6F

was highly improved when the exchanged zeolite was added to a paint containing reduced amounts of zinc phosphate. The employment of the modified zeolite allows the zinc phosphate content to be reduced by three times the values normally employed to formulate anticorrosive paints.[9–12]

Changes in wet adhesion at the steel–paint interface, in the salt spray chamber, are also shown in Table 3. The paint formulated with the modified zeolitic rock completely lost the adhesion to the substrate after 340 h, while the paint with zinc phosphate began to decrease the adherence beyond 340 h of exposure. In contrast, no adhesion loss was detected in the case of the paint with the modified zeolite and zinc phosphate during the whole test period (840 h).

Only the paint formulated with the modified zeolite and zinc phosphate blistered in the humidity chamber after 20 days, although no corrosion spots were observed on the surface. This revealed the inhibitive action of the pigment's mixture. In contrast, the other paints showed no blisters but did show rusting on the surface after 500 h (see Table 4).

Results of electrochemical tests on painted panels

The corrosion potential of painted steel panels was measured in 0.5 M sodium perchlorate, as a function of time (see Fig. 5). The worst anticorrosive performance was observed for panels coated with the paint containing zinc phosphate (Paints 2). After 2 days of immersion, the corrosion potential of these specimens began to drop to match typical values of painted steel undergoing corrosion. Panels coated with the alkyd

Table 4: Degree of paint rusting and blistering in the humidity chamber

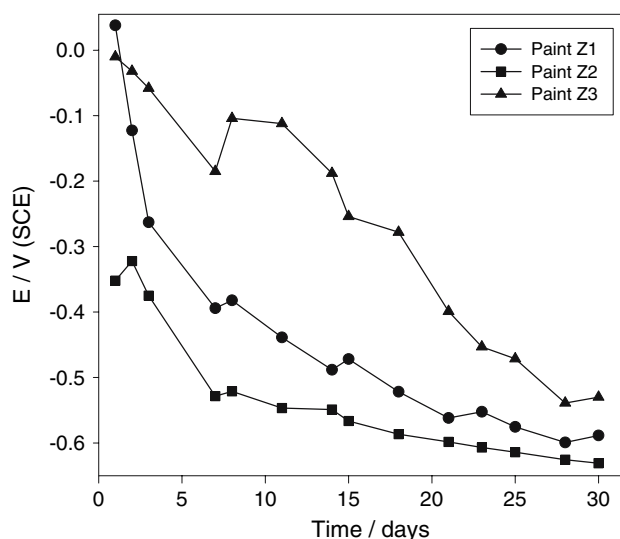| Paint	Hours			
	500		840	
	Rusting	Blistering	Rusting	Blistering
Z1	7	10	6	10
Z2	8	10	7	10
Z3	10	7 MD	10	6 MD

Fig. 5: Corrosion potential of painted panels

paint pigmented with the modified zeolite showed a better performance because they exhibited positive corrosion potential values and maintained values higher than at least –400 mV during 10 days of immersion. The observed behavior for the paint containing both inhibitors was noticeable because the measured corrosion potential values were higher than –300 mV for 3 weeks, thus indicating the existence of a synergy between both pigments that resulted in improved anticorrosive protection. In addition, the repassivation of the substrate was observed between the first and the second week of immersion while it was slightly visible compared to the other paints. This is an unusual behavior in an alkyd anticorrosive paint that, as a general rule, presents a behavior similar to the paint formulated with zinc phosphate alone. This essay showed, at first, the advantage of substituting two-thirds of zinc phosphate with the modified zeolite, with a corresponding savings.

None of the tested paints developed a significant barrier effect because their ionic resistance was lower than $10^6 \ \Omega \ cm^2$ (see Fig. 6). As it happens with all alkyd paints, the ionic resistance diminished after the first day of immersion and maintained rather low values during the test period. The behavior of the paint
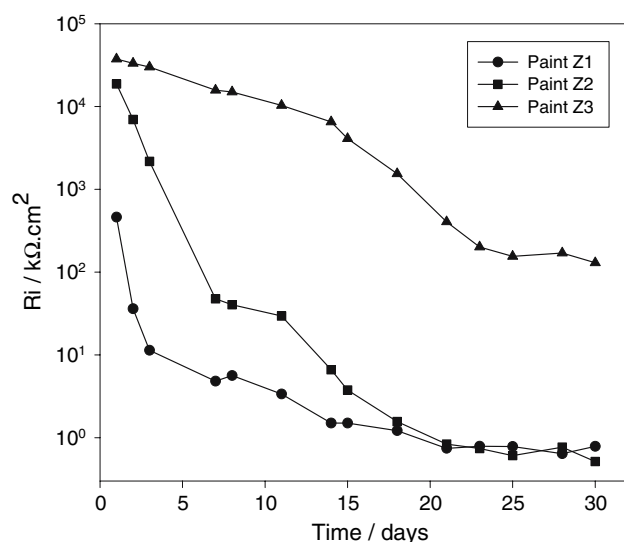
Fig. 6: Ionic resistances of painted panels

containing zinc phosphate was slightly better than the paint with the exchanged zeolite. The barrier properties of the paint containing zinc phosphate and the modified zeolite (Paint 3) was superior to the rest of the coatings in the sense that it maintained a rather high value of this parameter during 10 days of essay and decreased more slowly than the others. The ionic resistance of this paint's films was, on average, higher than $10^4 \ \Omega \ cm^2$ and higher than the two other paints. This fact was attributable to a better packing of the submicrometric zeolite particles and the micrometric zinc phosphate particles. The ionic resistance of a coating depends on the conductive paths in the film, especially those reaching the metallic surface, and it decreases as the number of these paths increase. The porosity of the paint film, defined as the quotient between the free volumes in the film (voids) that are occupied by air and the total film volume, decreases as the free volume in the film decreases. The packing factor increases as the free volume decreases.[58] It is thought that the presence of the zeolite nanoparticles combined with other microparticles leads to closer particle packing, thus reducing the voids that could easily generate these conductive paths in the film and increase its ionic resistance.

It is obvious from the preceding discussion that the protection afforded by these paints did not rest upon the barrier properties of the film but on the action of the anticorrosive pigments. In particular, the combination of the exchanged zeolite and zinc phosphate produced clearly advantageous results.

As a general rule, it can be said that the polarization resistance of the three paints was higher than the ionic, showing that corrosion was inhibited. The inhibition was stronger in the case of Paint Z3, due to the combined action of the zeolitic rock and zinc phosphate.

Conclusions

1. The modified zeolite exchanged with molybdenyl ions is effective to protect steel from corrosion when is used in combination with zinc phosphate.
2. A synergism exists between the exchanged zeolite and phosphate ions.
3. The employment of the modified zeolitic rock allows a reduction in zinc phosphate content, with a consequent savings.
4. The very good performance of the paint containing the modified zeolite and zinc phosphate can be attributed not only to the inhibitive properties of the pigments but also to the improved particle packing obtained with the submicrometric zeolitic rock.

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