



The assessment of a smart anticorrosive coating by the electrochemical noise technique

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ABSTRACT

Zinc phosphate and related compounds are convenient replacements for chromates. However, more eco-compatible pigments are being investigated. The objective of this research was to develop a modified zeolitic rock which is intended to replace phosphate pigments in anticorrosive paints. The modified zeolitic rock was obtained by grinding the rock followed with ionic exchange with molybdenyl ions. This “composite” has an intelligent behavior because molybdenum compounds are leached from the zeolite particle by corrodent species. The anticorrosive properties of this zeolitic rock were studied by electrochemical techniques, employing inhibitor suspensions, and formulating anticorrosive coatings. Coatings performance was evaluated by accelerated tests (humidity chamber and salt spray) and electrochemical noise measurements (ENM). Electrochemical noise data were analyzed in the time domain. The noise resistance (R_n) was compared, as far as possible, with the polarization resistance.

It was demonstrated that zinc phosphate content could be reduced to one-third with respect to the recommended value in the literature. The electrochemical noise technique allowed to differentiate the anticorrosive performance of the different coatings formulated in this research.

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1. Introduction

From 1970 on, two major goals were 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's regulations. Traditional anticorrosive paints contain lead or hexavalent chromium compounds as active pigments, which contaminate the environment and, at the same time, represent a risk to human health. Many compounds have been suggested as possible replacements for chromates and lead compounds but zinc phosphate and related substances became the leading substitutes for toxic inhibitors. Three generations of phosphates were introduced in the market, being zinc phosphate the precursor [1–10]. The second generation was developed by performing suitable modifications in the zinc phosphate particle [7–14]. Finally, the third generation was designed to meet high technological applications and was obtained changing the orthophosphate anion by the tripolyphosphate one [15–25]. Both, the second and third generation phosphate pigments are claimed to have equal or superior anticorrosive behavior than chromates and better than zinc

phosphate on its own. However, some concerns have risen in the last years because the disposal of these materials in the environment increased phosphate levels in water and produces eutrophication of the water bodies. Zinc was also considered as a contaminant with certain toxic effects [26,27] and, as a consequence, the European Community restricted the employment of zinc [28]. So, despite zinc phosphate is much less toxic than lead or hexavalent chromium compounds, it needs to be replaced.

Taking into account the inconveniences originated by the employment of zinc phosphate and related compounds, other strategies have been developed to replace zinc phosphate or, at least, diminish its content in anticorrosive paints. One of them consisted in the employment of more effective complementary pigments such as zinc oxide or silicates to obtain the same performance, but with lower anticorrosive pigment content. In this sense, natural silicates such as wollastonite and mica have been available for many years but, recently, they have gained increasing acceptance due to suitable surface treatment to improve their performance [29,30].

More recently, the challenge in the field of paint technology is to formulate smart coatings which are structured coating systems that provide an optimum selective response to some external stimulus such as temperature, stress, strain, corrosion, etc. Their smart behavior results from scientific combination of intrinsic coating properties and the incorporation of nanotechnologies. Ideally, a smart corrosion inhibitive coating will generate or release an

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inhibitor only when demanded by the initiation of corrosion. In this sense, different types of smart coatings were proposed in the literature such as paints formulated with ion-exchanged pigments, conducting polymers, self-healing coatings, etc. [31].

Zeolites (Z) possess interesting properties such as the ability of exchanging cations; so it is possible to exchange them with passivating cations which may play a role in steel protection once they are released from the zeolite by aggressive species [32–35]. Besides, zeolites are not toxic and represent no risk to the environments; they are frequently used in the food industry.

The objective of this research was to develop a modified zeolitic rock (from now on called MZ) which is intended to replace phosphate pigments in anticorrosive paints. MZ was obtained by ionic exchange with molybdenyl ions. Molybdenyl ions are readily converted into molybdate ions which has good inhibitive properties [36–42]. The anticorrosive properties of MZ were studied by electrochemical techniques, employing inhibitor suspensions, and formulating anticorrosive coatings. Coatings performance was evaluated by accelerated test (humidity chamber and salt spray) and electrochemical noise measurements. The MZ proved to be effective to protect steel from corrosion when is used in combination with zinc phosphate. Moreover, a synergism between the MZ and the phosphate ions was detected which may it possible to reduce the zinc phosphate content in paints. In a previous paper it was demonstrated that zeolites by themselves do not inhibit steel corrosion. In change, the inhibitive properties of molybdenum compounds are well known, as it was said previously.

Electrochemical noise measurements (ENM) can be used for ranking high-impedance coating systems and its use has already been well documented elsewhere [43–45]. The most common cell for ENM is constituted by three electrodes: two painted panels prepared exactly in the same way (joined together during measurement via a zero resistance ammeter) and a reference electrode. The three electrodes are placed in the same container with an electrolyte solution to easily control temperature fluctuations. The container is placed in a Faraday's cage. The experimental arrangement is a computer-controlled, automated digital system for the simultaneous measurement of electrochemical voltage and current, as described elsewhere [46]. Adequate filtering is provided just to eliminate line signals and aliased signals [47,48]. Statistical analysis of each time series is performed and the noise resistance (R_n) is calculated as the quotient $R_n = \sigma_E / \sigma_i$ [47–50] being σ_E the dispersions of the potential data and σ_i the dispersion of the coupling current.

It was demonstrated that the employment of MZ allowed to reduce zinc phosphate content to one-third with respect to the value recommended in the literature [6,9,10].

2. Materials and methods

2.1. Pigment preparation and characterization

A natural zeolitic rock, rich in the sodium zeolite, called clinoptilolite (93.3%), characterized in previous research [35], was selected, ground, heated and, finally, modified by ionic exchange with a molybdenum cation (MoO_2^{2+}). Apart from the zeolite (Z), the rock contained quartz (2.3%) and feldspars (4.4%). As it was stated, the rock was ground to obtain a fine grained powder (0.4–0.8 μm , 95%) and heated at 350 °C during 4 h, allowing it to cool in the furnace overnight. The preparation of MZ was carried out in a beaker where the ground rock was brought into contact with the molybdenyl solution. The molybdenyl solution was prepared dissolving 10 g molybdic acid in 90 ml of 1 M sulfuric acid, according to the following reaction:

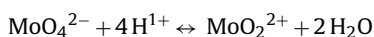
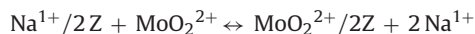


Table 1
Composition of the paints (% by volume).

| 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 sulphate | 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 |

Chemicals employed in this investigation were reagent grade ones from Merck. Considering the sodium zeolite, $2\text{Na}^+/2\text{Z}$, the ionic exchange reaction could be written as:



The suspension of MZ was kept at room temperature for 24 h with continuous stirring to be finally filtered by vacuum. The solid was washed several times with distilled water and one last time with a 0.01 M sodium acid carbonate solution to eliminate any residual acidity. MZ was dried at room temperature until constant weight. The capacity of the zeolitic rock for ionic exchange was measured using an ammonium salt solution, as suggested in the literature [51] and it was found to be equal to 4.4 mequiv. of cation per 100 g of zeolite.

A commercial zinc phosphate, PZ20, purchased from Societé Nouvelle des Couleurs Zinciques, was selected to prepare the paints used in this research. Its composition was obtained by dosing the phosphate and the zinc contents, employing conventional analytical procedures, and its anticorrosive behavior was checked in previous research [29].

2.2. Evaluation of the inhibitive properties of pigment suspensions

The corrosion potential of SAE 1010 steel, employing a saturated calomel electrode (SCE) as reference, was measured in the following pigment suspension: (a) MZ, (b) zinc phosphate and (c) MZ + zinc phosphate. Each suspension was obtained by dispersing 2 g of the corresponding pigment or pigment mixture in 0.025 M sodium perchlorate solution which was stirred for 24 h, previous to measurements, to allow its saturation. After 24 h, steel electrodes were dipped into the dispersion and measurements were carried

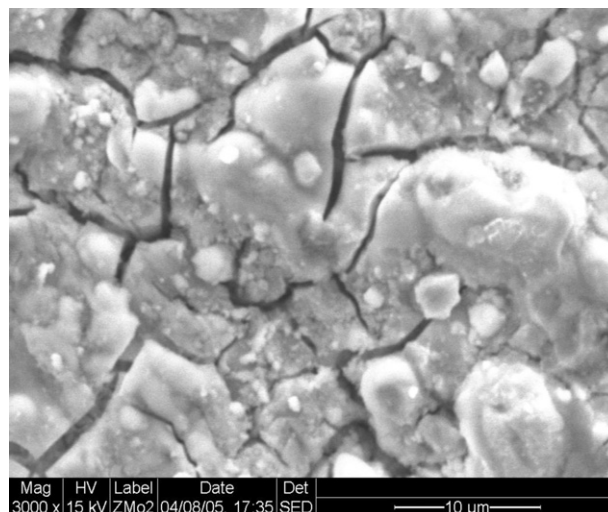


Fig. 1. SEM micrograph of film formed on the SAE 1010 steel panel in contact with the modified zeolite aqueous suspension (3000X).

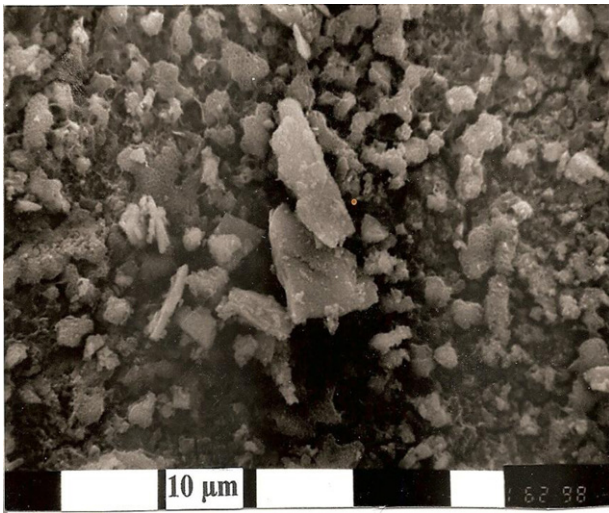


Fig. 2. SEM micrograph of film formed on the SAE 1010 steel panel in contact with the zinc phosphate aqueous suspension (2000X).

out. The exposed surface was finally observed by SEM (scanning electron microscopy) and the surface composition obtained by EDX (energy dispersive analysis of X-ray).

Anodic and cathodic polarization curves of an iron electrode were obtained after 6 h of exposure, employing the pigment suspensions and the supporting electrolyte described in the foregoing section. The suspension was stirred at 300 r.p.m. to avoid pigment settlement. A SCE was used as reference and a platinum grid as the counter-electrode. The swept began in the vicinity of corrosion potential, at a scan rate of 1 mV s^{-1} .

2.3. Paints composition, manufacture and application

The resin used to form the paint films to carry out this research was a medium oil alkyd (50% linseed oil, 30% *o*-phthalic anhydride, 8% pentaerythritol and glycerol and 12% pentaerythritol resin), provided by POLIDUR S.A., and the solvent was white spirit.

The paints contained different loadings of anticorrosive pigment in order to study the anticorrosive behavior of MZ. Paint 1 had 30% by volume of MZ with respect to the total pigment content, paint 2 has 10% of zinc phosphate, a common anticorrosive pigment and

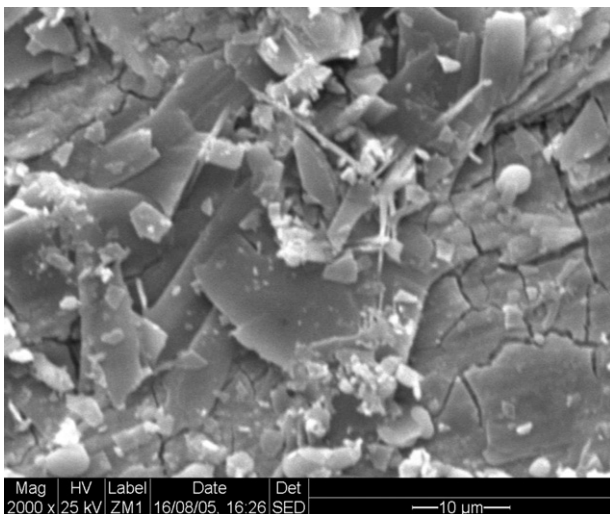


Fig. 3. SEM micrograph of film formed on the SAE 1010 steel panel in contact with the modified zeolite + zinc phosphate aqueous suspension (3000X).

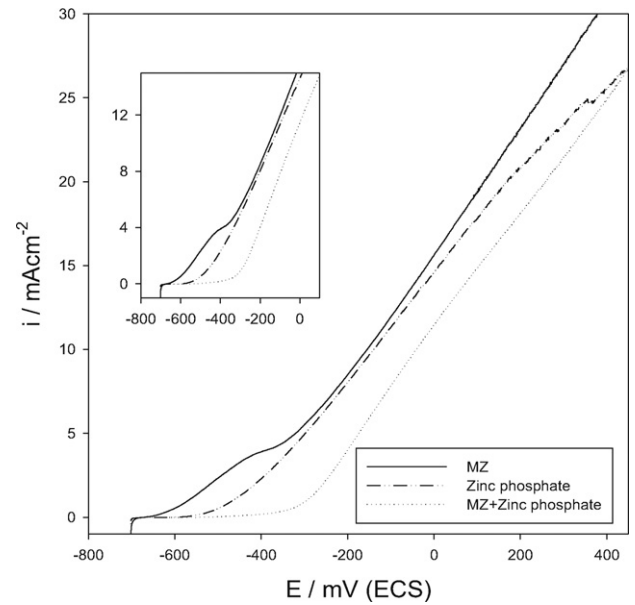


Fig. 4. Polarization curves of SAE 1010 steel in contact with the modified zeolite suspension, zinc phosphate suspension, the modified zeolite suspension + zinc phosphate: (a) anodic curves and (b) cathodic curves. Scan rate 1 mV s^{-1} .

paint 3 has 10% of zinc phosphate and 20% of MZ. Titanium dioxide, zinc oxide and barium sulphate were incorporated to complete the pigment formula. Paints composition could be seen in Table 1. The pigment volume concentration/critical pigment volume concentration (PVC/CPVC) relationship was 0.8. Pigments were dispersed in the vehicle employing a ball mill with a 3.3 l jar for 24 h to achieve an acceptable dispersion [52].

SAE 1010 steel panels ($15.0 \text{ cm} \times 7.5 \text{ cm} \times 0.2 \text{ cm}$) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene and then painted, by brush, up to a dry film thickness of $75 \pm 5 \mu\text{m}$. Painted panels were kept indoors for 7 days before being tested.

2.4. Accelerated laboratory tests

A set of three panels was put in the salt spray chamber (ASTM B 117) to evaluate the rusting (ASTM D 610) and blistering (ASTM D 714) degrees, after 340, 840, 1500 and 2300 h of exposure. The adhesion of the coatings to steel was measured by the tape test

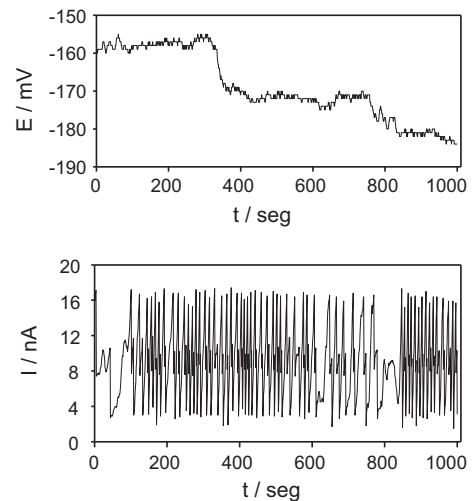


Fig. 5. Typical noise spectra of paint Z3 after 196 h of exposure: (a) potential and (b) coupling current.

Table 2
Rusting and blistering degree and failure at the scribe for the alkyd paints in the salt spray cabinet.

| Paint | Time (h) | | | | | | | | | |
|-------|----------|----------|---------|------------|----------|---------|------------|---------|------------|--|
| | 0 | 340 | | | | 840 | | | 1500 | |
| | Adhesion | Adhesion | Rusting | Blistering | Adhesion | Rusting | Blistering | Rusting | Blistering | |
| Z1 | 5B | 0B | 6 | 4MD | – | – | – | – | – | |
| Z2 | 5B | 5B | 8 | 10 | 0B | 6 | 6D | – | – | |
| Z3 | 5B | 5B | 10 | 10 | 5B | 9 | 10 | 8 | 6F | |

(ASTM D 3359) after 340 and 840 h exposure in order to be compared with the values obtained before placing the panels into the salt spray chamber.

Another set of panels was put in the humidity chamber (ASTM D 2247) and evaluated after 500 and 840 h. The blistering and the rusting degrees were established as mentioned above.

The cell for ENM was constituted by two identical painted panels; the edges of these panels were blanked off being the exposed area 50 cm². The SCE was employed as reference. The three electrodes were dipped into a 0.5 M NaCl solution and monitored continuously. Adequate filtering was provided just to eliminate line signals and aliased signals [47,48]. The sensitivity of the measuring device in the *E*-scale was 100 μV and 0.1 nA in the current measurements. The sampling frequency was 1 Hz, which is commonly used to study corroding systems. Each time series contained 1000 points.

The noise resistance (R_n) was calculated as $R_n = \sigma_E / \sigma_i$ [47,48,50]. Although the mean values of raw data were plotted, the d.c. trend was removed to perform R_n calculation by the moving average removal procedure described by Tan et al. [53].

R_n was compared with the polarization resistance which was determined employing a three electrode cell when the paint film resistance was below 10⁵ Ω cm². The painted metal was the working electrode; a SCE was used as reference and a platinum grid as the counter-electrode. The sweep amplitude was ±20 mV from the corrosion potential and the scan rate 1 mV s⁻¹. Measurements were carried out with a Potentiostat–Galvanostat EG&G PAR Model 273A plus SOFTCORR 352 software. It was decided to determine the polarization resistance in a separate experiment in order not to disassembly the cell for ENM each time this magnitude was measured.

3. Results and discussion

3.1. Evaluation of the inhibitive properties of pigment suspensions

The corrosion potential of the steel panel in contact with MZ was –647.5 mV (ECS) after 24 h of immersion in 0.025 M NaClO₄.

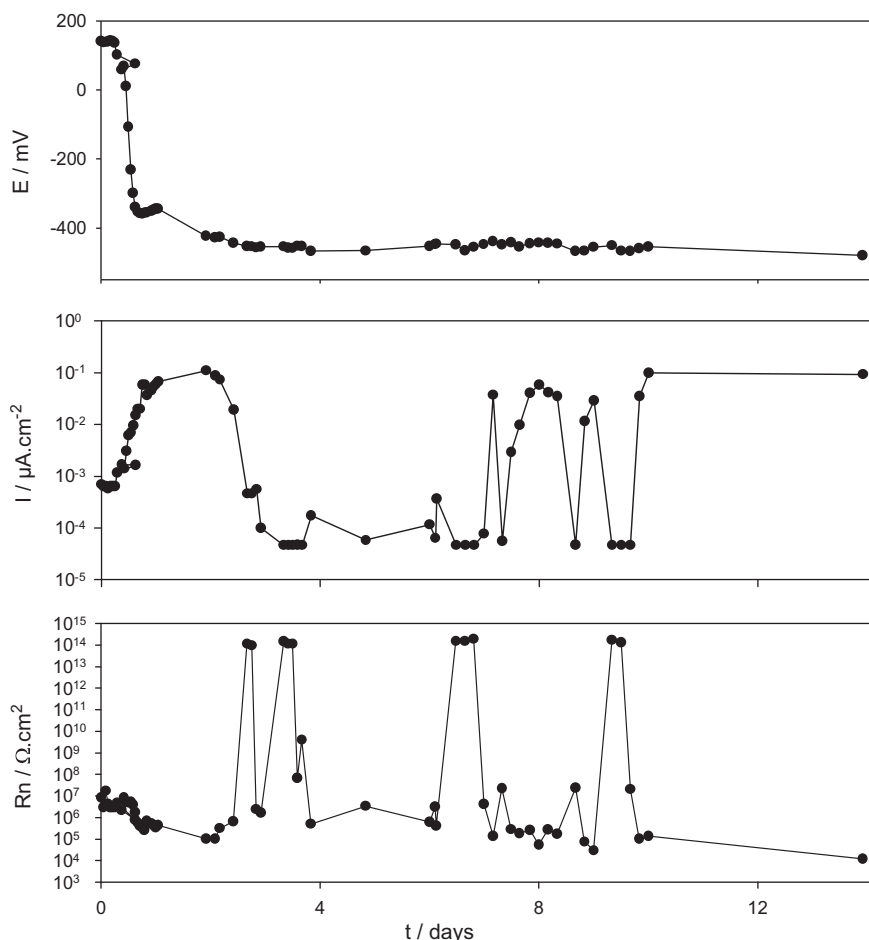
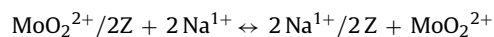
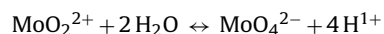


Fig. 6. Statistical analysis of noise data of paint Z1: (a) mean noise potential; (b) mean coupling current; (c) noise resistance (R_n).

The protective layer appeared to be a cracked and non-protective film with small spherical formations embedded in it (Fig. 1). Molybdenum concentrated in these spheres (92.3% of MoO_3) which contained very low amounts of iron (7.7% as Fe_2O_3). The gel-like formation was also rich in molybdenum. These findings confirmed that MZ really acted as a smart pigment because the molybdenum species, which were initially retained in the zeolite, now appeared onto the metallic surface [31,54]. Molybdenum ions were liberated to the corrosive environment by cations present in the aggressive medium, such as sodium from sodium chloride:



In addition molybdenyl ion is converted into molybdate anion in the aggressive medium:



The corrosion potential of the steel panel in zinc phosphate in 0.025 M NaClO_4 was -503.4 mV (ECS), but no corrosion signs appeared on its surface. The protective layer, observed by SEM, was constituted by a base film composed by iron oxyhydroxides (>75%) which may contain, eventually, zinc oxide (Fig. 2). The globular formations, which were supposed to plug pores in the base film [1,6,30], contained higher amounts of phosphorous oxide (>6%) and zinc oxide (>45%).

The corrosion potential of the steel panel in the presence of the modified zeolite and zinc phosphate was found to be -679.6 mV (ECS). As in the previous case no corrosion signs were detected on the metallic surface. The protective film was constituted by two

Table 3

Rusting and blistering degree of the paints in the humidity chamber.

| Paint | Hours | | | |
|-------|---------|------------|---------|------------|
| | 500 | | 800 | |
| | Rusting | Blistering | Rusting | Blistering |
| Z1 | 7 | 10 | 6 | 10 |
| Z2 | 8 | 10 | 7 | 10 |
| Z3 | 10 | 7MD | 10 | 6MD |

layers. The first layer was a more or less uniform film with big crystals and plates grown on it. The bare layer was mainly constituted by iron oxide. The composition of crystals and plates was rather complex and similar in nature. The main constituents were P_2O_5 (26.4%) and ZnO (53.8%) with smaller amounts of FeO (17.5%) and MoO_3 (2.3%) (Fig. 3). From these results, it seemed that molybdenum allowed a better phosphating of the bare metal.

The highest anodic current was observed for the iron electrode in MZ suspension. The behavior of the iron electrode in the zinc phosphate suspension was similar but current diminished at higher potentials. The lowest current was measured for the iron electrode in the suspension containing MZ and zinc phosphate (Fig. 4a). At lower potentials, the dissolution of the steel electrode in this suspension appeared to be quite inhibited in a wide potential interval (Fig. 4a). According to the previous discussion, zinc phosphate resulted a little more effective than MZ in inhibiting steel dissolution but the combination of both inhibitors led to much better

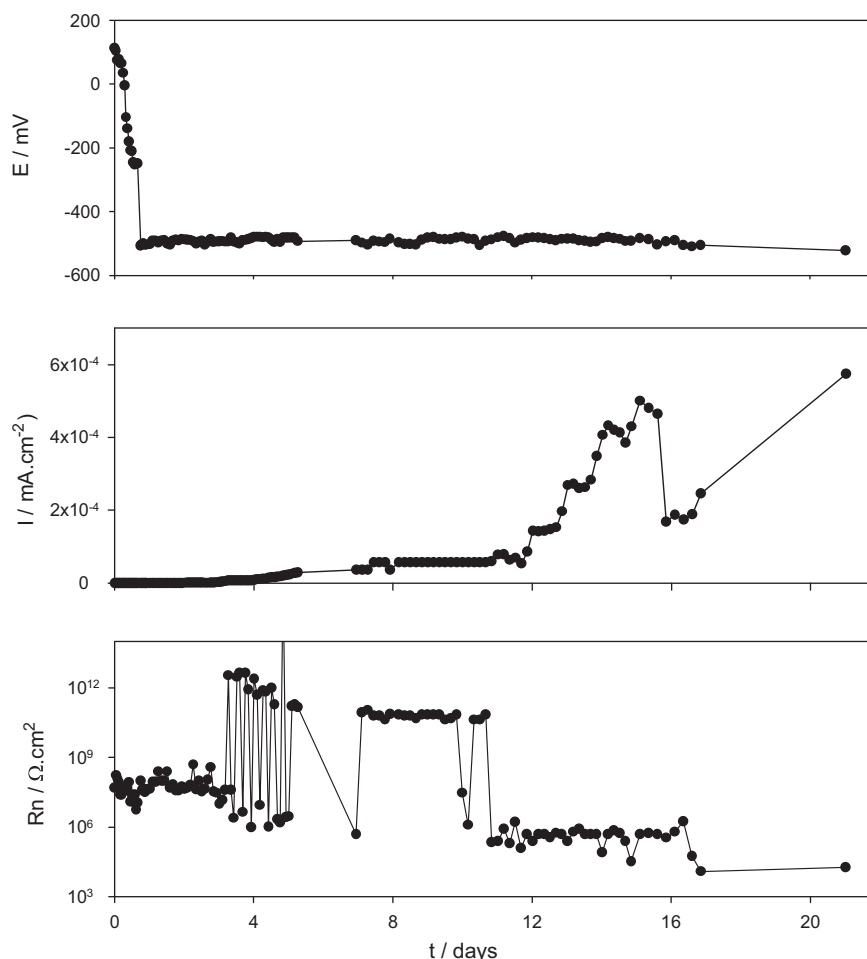


Fig. 7. Statistical analysis of noise data of paint Z2: (a) mean noise potential; (b) mean coupling current; (c) noise resistance (R_n).

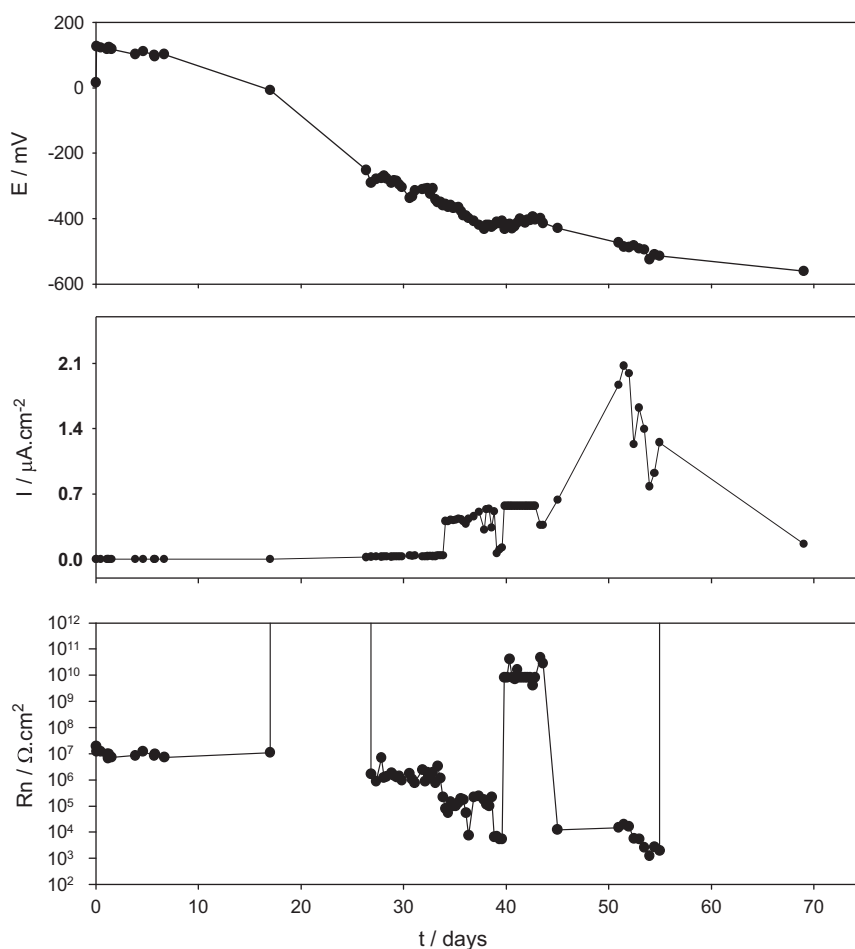


Fig. 8. Statistical analysis of noise data of paint Z3: (a) mean noise potential; (b) mean coupling current; (c) noise resistance (R_n).

results than either one alone; that is to say there is a synergism between both types of inhibitors.

The cathodic polarization curve obtained with MZ did not show evidence of corrosion inhibition because the oxygen current was not diminished by the pigment (Fig. 4b). However, cathodic current diminished in phosphate suspensions, but the lowest values were observed in the presence of MZ plus zinc phosphate (Fig. 4b).

3.2. Accelerated laboratory tests

Results obtained in the salt spray cabinet are shown in Table 2. The paint Z1, without zinc phosphate, had a disappointing behavior because it cannot surpass 340 h of exposure; corrosion spots and blisters appeared during the second week of essay. The degradation of the paint containing zinc phosphate (Z2) could be clearly appreciated after 840 h while the paint with zinc phosphate and MZ (Z3) showed, at that moment, very few rusting points and no blisters. The panels coated with this paint underwent 1500 h of exposition with a good qualification (rusting degree 8) which dropped to 7 after 2300 h. The most important conclusion derived from this experiment is that the anticorrosive behavior of paints was highly improved when the modified zeolitic rock was added to a paint containing reduced quantities of zinc phosphate.

Changes in paint wet adhesion in the salt spray cabinet are also shown in Table 2. The paint formulated with MZ lost completely the adhesion to the substrate after 340 h while the paint with zinc phosphate began to decrease the adherence beyond 340 h. On the

contrary, no adhesion loss was detected in the case of the paint with MZ and zinc phosphate during the 840 h of exposure.

Only the paint with MZ and zinc phosphate blistered in the humidity chamber, after 20 days, although no corrosion spots were observed on the surface. The other paints had no blisters but rusting appeared on the surface after 500 h (Table 3).

3.3. Results of electrochemical tests on painted panels

Preliminary results reported in the literature indicate the applicability of ENM to assess coatings anticorrosive performance even in high impedance systems. It was demonstrated that R_n values as high as $10^{10} \Omega \text{ cm}^2$ or even greater could be measured in heavy duty paints by the EN technique [43–45,54–56]. These previous statement will be confirmed in this research. In addition, it will be shown that if raw mean noise potential and mean coupling current values are plotted against time, the polarization of the painted metal could be described adequately. Typical noise potential spectra (a) and noise coupling current spectra (b) can be seen in Fig. 5.

Results obtained with the paint Z1, containing MZ, are presented in Fig. 6. Mean noise potential of panels coated with paint Z1 descended and the coupling current increased, during the first hours of exposure, indicating that steel dissolution was taking place leading to the formation of a protective layer. The noise resistance showed values oscillating in the range 10^5 to $10^7 \Omega \text{ cm}^2$. Afterwards, the coupling current as well as the noise potential decreased while the values of the noise resistance maintained high and oscillating; probably indicating the inhibition of the electrochemical reaction. It is thought that during this period the protective layer

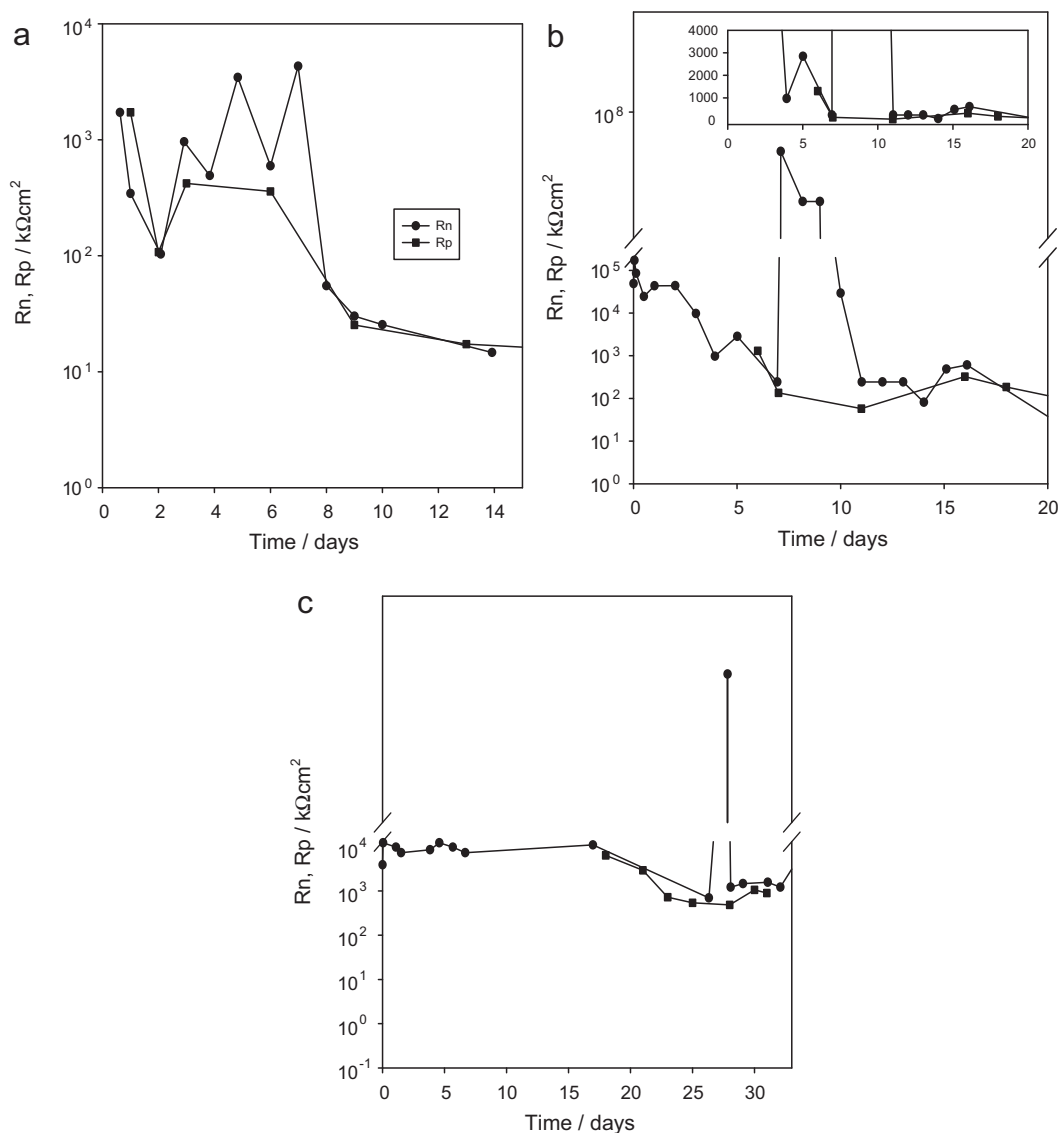


Fig. 9. Comparison between the noise resistance (R_n) and the apparent dc polarization resistance (R_p): (a) paint Z1; (b) paint Z2; (c) paint Z3.

formed under the paint film increased its thickness without changing its nature; it also seemed that the breakdown and film repair took place as it could be deduced from the shape of the I vs time plot. During this period no signs of corrosion were observed on the paint film. No significant changes in the mean values of noise potential were detected between 4 and 6 days and R_n remained low.

After 6 days and up to 10 days of exposure strong oscillations in the value of the coupling current were observed accompanied by lower amplitude oscillations in the noise potential. Finally oxide spots grew on the steel surface; R_n values, concomitantly, remained low. After 10 days the noise potential decreased and the coupling current maintained high while R_n acquired the lowest values of the whole test period; it is obvious that the corrosion process generalized over the entire surface.

The mean values of the noise potential of the paint pigmented with zinc phosphate (Z2) decreased after 24 h of exposure to finally match -500 mV (SCE) which maintained almost constant during the whole test period (Fig. 7). The coupling current increased slowly during this period and R_n oscillated, approximately, between 10^2 and $10^{12} \Omega cm^2$. After 12 days of testing the coupling current increased although the noise potential did not change significantly.

It seemed that a certain protective layer was formed during the first hours of immersion which changed slightly during 12 days. After this period the system tried to passivate but current increased after 16 days of exposure and the noise resistance decreased.

The electrochemical behavior of the steel coated with the paint Z3 containing MZ and zinc phosphate was quite different to the other paints, as it could be appreciated from the evolution of the mean parameters as time elapsed (Fig. 8). The noise potential exhibited positive values for more than 10 days, being almost constant during the first week of immersion and maintained higher than -300 mV (SCE) for almost 25 days, thus indicating the protection of the steel substrate. After 25 days of exposure, the noise potential continued decreasing up to 35 days, although the coupling current showed very low values from the very beginning of the test period. After 35 days the coupling current increased and reached its maximum value after 50 days of exposure to finally decay to very low values after 70 days of exposure. The R_n values varied jointly with the other parameters, it presented high values during the first 25 days of immersion, probably due to the formation of a protective layer which changed slightly in nature to form corrosion products which disrupted through the paint film after this period. During the breakdown of passivity the R_n values were

lower and oscillated to increase when repassivation was achieved again.

R_n of the bare metal was very low ($>50 \Omega \text{ cm}^2$) while R_n of coated metals, particularly at the end of the immersion period, was still higher than that of the substrate in the supporting electrolyte. This led to the conclusion that coated metal continued protected in some way; but it would be more desirable that R_n surpassed $10^6 \Omega \text{ cm}^2$ as it is requested for the polarization resistance. However, a more accurate comparison needs the electrochemical active area to be determined.

Finally, the noise resistance was compared with the apparent polarization resistance, measured without IR compensation (Fig. 9). As a general rule it may be said that the noise resistance varied jointly with the apparent polarization resistance when two identical electrodes were employed and the electrochemical reaction is under activation control [57–59]. However, several researchers believed that the similarity between R_n and R_p did not hold for every system [60,61]. Results confirmed the similarity of R_n with the “apparent” polarization resistance. The question is that the d.c. polarization resistance could not be measured accurately if it surpassed $10^4 \Omega$ due to intrinsic limitations of the measuring device while the noise resistance was measured from early times, in spite of its high values, thus giving a more accurate description of the behavior of the anticorrosive paints. It also seemed that R_n was more sensitive to changes in the electrochemical interface because it can oscillate between very high and low values. The foregoing discussion points out that the electrochemical noise technique is a very sensitive tool to explore the behavior of the metal/paint interface.

4. Conclusions

1. Salt spray and electrochemical tests showed that two-thirds of zinc phosphate could be replaced by a zeolitic rock modified with molybdenum compounds.
2. There exists a synergism between the modified zeolitic rock and zinc phosphate which allowed a better phosphatization of the base metal.
3. The electrochemical noise technique resulted useful to differentiate the anticorrosive performance of tested paints.
4. The noise resistance could be compared with the apparent polarization resistance and may be related to paint anticorrosive performance.

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