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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.

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:

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

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, $2\,Na^{1+}/2\,Z$, the ionic exchange reaction could be written as:

$$Na^{1+}/2\,Z + MoO_2^{2+} \leftrightarrow MoO_2^{2+}/2Z + 2\,Na^{1+}$$

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

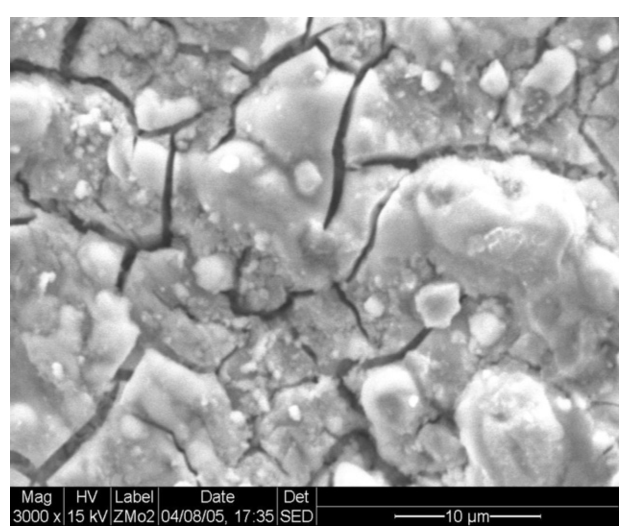

Fig. 1. SEM micrograph of film formed on the SAE 1010 steel panel in contact with the modified zeolite aqueous suspension (3000X).