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Evaluation of eco-friendly anticorrosive pigments for paints in service conditions

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ABSTRACT

The performance of different replacements for chromates was studied. The anticorrosive properties of seven phosphate-based pigments, a calcium-exchange silica and a ferrite were assessed by electrochemical techniques and formulating solvent-borne paints with epoxy and alkyd resins. Paints contained 30% by volume of anticorrosive pigment, with respect to the total pigment content.

The anticorrosive performance of paints was evaluated by accelerated tests (salt spray chamber) and electrochemical essays (corrosion potential and ionic resistance). Outdoor exposure tests were carried out in an urban-industrial environment during 8 years.

The anticorrosive performance of the tested paints showed that there is not a clear relationship between the laboratory tests and the outdoors exposition and that none of them, by themselves can predict the behaviour of the paint under service. However, electrochemical essays with pigments may give an orientation about pigment performance in anticorrosive paints. As a general rule, if the pigment reduces notably steel corrosion rate and generates a rather high apparent polarization resistance a good anticorrosive performance may be expected.

1. Introduction

Organic coatings are a widespread method to protect steel against corrosion. Coatings protect metals from the adverse effects of atmospheric agents by two main mechanisms: a barrier effect and surface passivation. These two effects are in series, only after the coating is penetrated by water, oxygen and electrolytes, the anticorrosive pigments begin to act passivating the surface [1].

Classical anticorrosive paints normally contained inhibitors based on hexavalent chromium or lead compounds. The employment of these compounds is being restricted because they contaminate the environment and cause health problems to humans [2]. Regulations in different countries, led to an intense research to find out alternative pigments of low toxicity and with the same performance as the old ones.

The use of zinc phosphate in anticorrosive paints is widespread and has been well documented [3–7]. Although zinc phosphate gives good results, in certain cases, it proved to have lower anticorrosive performance than zinc chromate [4,5]. As a consequence, a second pigment generation based on zinc phosphate was introduced by modifying it with molybdenum or aluminium [4,8]. Finally, a third generation arose by substituting the phosphate anion by polyphosphates (tripolyphosphate, pyrophosphate, etc.) [9–17]. Both pigment series are claimed to have better anticorrosive behaviour than zinc phosphate.

Although phosphate pigments dominate the market, many other inhibitors were developed for improved anticorrosive protection. Ferrites and ion-exchange pigments are acquiring increasing importance as alternative products. These inhibitive substances have not been studied as deeply as phosphates; but, in many accelerated tests they exhibit better performance than zinc phosphate [10,18–24].

Ferrites have the general formula XFe_2O_3 (X = MgO, ZnO or CaO) or YAl_2O_3 (Y = CaO, ZnO) and a spinel structure [10,18–20]. Ferrites can act as barrier pigments or by neutralizing the action of corrosives substances that diffuse through the coating [21]. In this last case, the reaction between the fatty acids present in the resin and the anticorrosive pigment forms soaps which harden and seal the coating. Besides, the metallic substrate is passivated by the alkaline media generated by the hydrolysis of the pigment [10].

The protection of the metallic surface by paints with exchange pigments is claimed to be due to the growth of a silica film onto the metal surface and calcium ions, exchanged from silica particles, which migrate towards the metal-coating interface. The resulting film is impermeable to humidity and ions, preventing corrosion. However, it seems that protection depends more on the high pH provided by the pigment than on other of its properties [23–27].

The protective ability of coatings is currently evaluated by electrochemical and accelerated essays. These last ones often simulate extreme environments such as the marine one or high humidity environments. However, in most cases, there is not a good cor-

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Table 1
Anticorrosive pigments main chemical composition.

Pigment		Chemical composition (% by weight)
ZP	Zinc phosphate	36.3% zinc, 52.5% phosphate, 8.7% de sodium; $Zn_3(PO_4)_2$
ZMP	Zinc molybdophosphate	43.7% zinc, 35.4% phosphate, 0.26% molybdenum
Zpp	Zinc polyphosphate	24.4% zinc, 47.6% phosphate and 2.1% sodium; $NaZn_2(P_3O_{10})$
Capp	Calcium polyphosphate	22.3% calcium, 69.7% phosphate, 2.3% sodium; $NaCa_2(P_3O_{10})$
Alpp	Aluminium polyphosphate	3.4% aluminium, 24.3% zinc, 8.2% silica; 64.1% phosphate
ZPy	Zinc pyrophosphate	31.7% zinc, 49.4% phosphate, 0.7% de sodium; $Zn_2(P_2O_7)$
ZHy	Zinc hypophosphite	69.7% zinc, 22.8% phosphate, 7.5% hypophosphite
CaEx	Calcium-exchange silica	5.25% calcium, 77.93% insoluble silica, 1.14% active silica
CaFt	Calcium ferrite	79.5% zinc, 20.0% calcium

relation between laboratory tests and the coating performance under service conditions. This lack of correlativity is due to the oversimplification made in accelerated tests about the aggressive environment where the coating will be exposed. Only a few variables such as high temperature, high humidity, presence of aggressive ions, U.V. radiation are normally taken into account in laboratory tests.

The aim of this work was to evaluate a selected series of corrosion protective pigments in outdoors conditions. The selected phosphate pigments were zinc phosphate (ZP), zinc molybdenum phosphate (ZMP), three different polyphosphates (zinc, calcium and aluminium tripolyphosphates, Zpp, Capp and Alpp, respectively), zinc pyrophosphate (ZPy) and a pigment based on zinc hypophosphite (ZHy). As alternative non-phosphate pigments, calcium-exchange silica (CaEx) and calcium ferrite (CaFt) were chosen. The results showed that accelerated and electrochemical tests are complementary and none of them by themselves can predict the behaviour of the paint under service (Table 1).

2. Experimental

The electrochemical behaviour of a SAE 1010 steel electrode in a suspension containing 5 g of the corresponding pigment in 0.025 M sodium perchlorate was studied. Steel corrosion potential was measured with respect to the saturated calomel electrode (SCE), during 4 h and after 24 h of immersion. Steel polarization resistance was also measured with (Rp^{IR}) and without IR-drop (Rp) compensation in a three electrode cell. The reference electrode was SCE and the counterelectrode a platinum grid. The sweep amplitude was ±20 mV, starting from the corrosion potential at a scan rate of 0.166 mV/s. Measurements were taken employing the 273A EG&G PAR Potentiostat/Galvanostat plus SOFTCORR 352 software.

Pigments performance was also assessed in anticorrosive paints. The materials used to form the paint films were an epoxy-polyamide resin and a medium oil alkyd (50% linseed oil, 30% o-phtalic anhydride, 8% pentaerytritol and glycerol, and 12% pentaerytritol rosinate) resin. The solvent mixture was xylene/methyl isobutyl ketone/butoxyethanol (13/45/42%) in the case of the epoxy resin and white spirit for the alkyd. The anticorrosive pigment concentration was, in every case, 30% v/v, with respect to the total pigment concentration. The complementary pigments were titanium dioxide, barium sulphate and talc. The composition of the pigment mixtures is shown in Table 2. The PVC/CPVC (Pigment Volume Concentration/Critical Pigment Volume Concentration) ratio 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 degree.

Paints were applied by brush on SAE 1010 steel panels (15.0 cm × 7.5 cm × 0.2 cm), previously degreased with toluene, up to a thickness of $80 \pm 5\ \mu m$.

A set of three panels was placed in the salt spray chamber (ASTM B 117). Rusting (ASTM D 610) and blistering (ASTM D 714) degrees were evaluated as a function of time.

Ionic resistance between the painted steel substrate and a platinum electrode was measured in the cell obtained by fixing an acrylic tube, 2 cm diameter, on the painted specimen and filling it with 0.5 M sodium perchlorate. Measurements were carried out employing an ATI Orion, model 170, conductivity meter at 1000 Hz. The corrosion potential was measured in the same cell, against SCE, with a high impedance voltmeter.

Another set of panels, with a suitable top-coat, total film thickness $100 \pm 5\ \mu m$, was placed at 45°, facing north, in the outdoor station of CIDEPINT, located at La Plata, Argentina (34°54′S and 57°55′W), in an urban-industrial environment. The characteristics of the station in terms of average temperature, relative humidity, winds and annual rain, according to the months and the years, are shown in Figs. 1–3.

Electrochemical measurements were also done on panels after 8 years of outdoor exposure. In this case, the samples were removed from the exposition site and the corrosion potential as well as the ionic resistance were measured employing the same cell described before. After the measurement, the samples were placed back outdoors.

3. Results and discussion

Results of electrochemical tests can be seen in Table 3. After 4 h of immersion, steel in contact with calcium polyphosphate had a corrosion potential more negative than that of the steel immersed in the supporting electrolyte (blank). The same results were obtained with calcium ferrite while in the case of aluminium and zinc polyphosphates, the corrosion potential was similar to the blank. However, only steel in the blank test rusted. This fact evidenced that the metal activity was similar in all these cases but the presence of the pigments induced the formation of a protective film [9,13]. The corrosion potential of the steel immersed in the other pigments' suspensions was at least 70 mV more positive than the blank and they never reached uncoated steel corro-

Table 2
Composition of the pigment mixtures (% by volume).

	Zp	ZMP	Zpp	Capp	Alpp	ZPy	ZHy	CaEx	CaFt
Anticorrosive pigment	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Titanium dioxide	12.0	12.0	14.4	14.4	12.0	12.0	12.0	12.0	14.4
Barium sulphate	29.0	29.0	36.1	36.1	29.0	29.0	29.0	29.0	36.1
Talc	29.0	29.0	19.5	19.5	29.0	29.0	29.0	29.0	19.5