



Anticorrosive water borne paints free from zinc and with reduced phosphate content



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ABSTRACT

The objective of this research was to formulate water-borne epoxy coatings free from zinc and with reduced phosphate levels, replacing zinc phosphate by calcium acid phosphate. Lanthanum molybdate was incorporated as a green anticorrosive pigment to enhance paint anticorrosive performance. Paints were assessed by accelerated (salt spray and humidity chambers) and electrochemical tests (ionic resistance and electrochemical noise).

Results suggested that zinc phosphate could be replaced by calcium acid phosphate and the phosphate content in the paint film reduced to one third. Lanthanum molybdate can act synergistically with phosphates.

1. Introduction

One of the most important challenges in the field of paint technology are concerned with the development of safer products, safer processes and reduced solvent emissions to the atmosphere with zero emissions as the most relevant achievement [1]. In the case of anticorrosive paints safer products means, primarily, the complete elimination of chromates and the employment of water instead of organic solvents. In this sense, from 1970 on, two major goals were achieved in the field of paint technology: the replacement of toxic inhibitive pigments containing lead and chromate compounds by phosphates and the progressive elimination of organic solvents in paint formulations to fit VOC's regulations.

Three generations of phosphates were introduced in the market, being zinc phosphate the precursor [1–11]. Zinc phosphate nanoparticles were reported to perform better than normal micrometric ones [12]. The second generation was developed by performing suitable modifications in the zinc phosphate particle [6–14]. Finally, the third generation was designed to meet high technological applications and was obtained changing the orthophosphate anion by the polyphosphate ones [15–25]. Both, the second and the third generation of phosphate pigments are claimed to have equal or superior anticorrosive behavior

than chromates and better than zinc phosphate on its own [26–29].

The synergism between phosphate based pigments has been studied. The interaction between molybdate and phosphate anions as well as zinc and/or calcium cation have been reported [3,7,8].

Other anticorrosive pigments, apart from phosphates, were found to be suitable to formulate anticorrosive paints. Among them, condensed phosphates [30], double phosphates of the formula $MM(PO_4)_n$, being M a metal cation [31], boron phosphates [32], calcium metaborate [32], ferrites [8,33,34], exchanged silicas and exchanged clays [34,35], anion exchange pigments [36], intrinsic conductive polymers [37,38], spinel-type compounds [30], etc.

Besides, anticorrosive pigments can act synergically as zinc phosphate and zinc hypophosphate.

The elimination of solvents was accomplished in different ways. One of the most important is concerned with the development of water-borne systems. These systems present a range of characteristic differences and, in some cases, difficulties not exhibited by solvent-borne paints [39–43]. It was stated everywhere that water-borne paints are less resistant to the corrosion process and prone to biological attack [40,44–47]. They also exhibit “flash rusting” during solvent evaporation which finally affects the appearance of the coating [44,47].

The objective of this research was to formulate water-borne coatings

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Table 1
Paints composition.

Components	1	2	3	4	5	6	7	Blank	Trademark
Lanthanum molybdate	0.6	0.6	0.6	–	–	3.6	–	–	Prepared in the laboratory
Calcium acid phosphate	0.6	1.8	3.0	1.2	2.4	–	3.6	–	
TiO ₂	3.1	2.8	2.4	3.1	2.8	2.4	2.4	3.4	Zamudio
Talc	3.0	2.6	2.3	3.0	2.6	2.3	2.3	3.3	Minera Cema
Mica	2.6	2.3	2.0	2.6	2.3	2.0	2.0	2.9	Minera Cema
Barium sulphate	2.0	1.8	1.6	2.0	1.8	1.6	1.6	2.3	Minera Cema
Resin	35.7	35.7	35.7	35.7	35.7	35.7	35.7	35.7	(Huntsman, Py340)
Curing agent (hardener)	29.8	29.8	29.8	29.8	29.8	29.8	29.8	29.8	(Huntsman, HZ340)
Distilled water	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	Prepared in the laboratory
Antifoaming	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	Diransa, Q202
Neutralizing amine	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	Dow, AMP-95

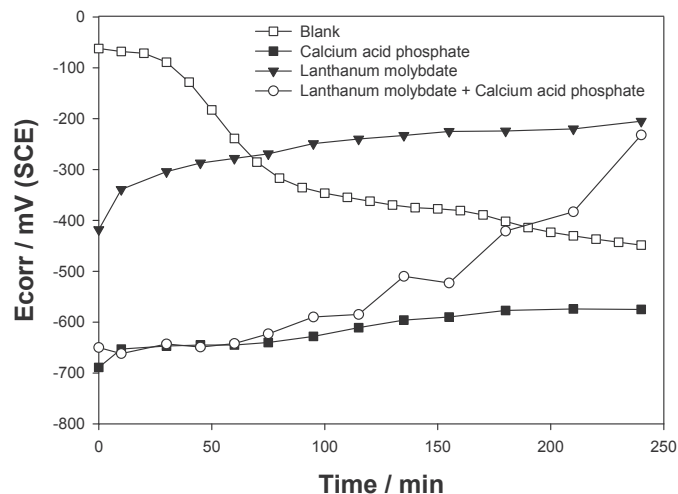


Fig. 1. Corrosion potential of steel immersed in different pigment suspensions.

free from zinc and with reduced phosphate levels. Zinc phosphate was completely replaced by calcium acid phosphate and lanthanum molybdate was added to enhance paint anticorrosive performance. Lanthanum molybdate was selected based on the successful employment of the analogue cerium molybdate while calcium phosphate was previously studied in our laboratory [48–50]. Lanthanides salts were successfully used as cathodic anticorrosion inhibitors to protect metals when exposed to an aggressive solutions, for protection at high temperatures [51], to improve the adherence of oxide films of different metallic alloys by ionic implantation, etc. [52,53]. Paints were assessed by accelerated tests (salt spray and humidity chambers) and ionic resistance and electrochemical noise measurements (ENM). ENM can be used for ranking high-impedance coating systems [54–56].

Results suggested that zinc phosphate could be replaced by calcium acid phosphate and the phosphate content in the paint film reduced to one third. Lanthanum molybdate can act synergistically with phosphates.

2. Experimental

Calcium acid phosphate was prepared according to a procedure described elsewhere [49,50]. Lanthanum molybdate was prepared by precipitation at pH 5.5 mixing two solutions: 2×10^{-3} M of lanthanum nitrate and 3×10^{-2} M sodium molybdate.

The stoichiometry of the final product was determined by means of current analytical techniques.

The corrosion potential of a SAE 1010 steel electrode was monitored, as a function of time, in the corresponding pigment suspension: 1 g of the pigment (lanthanum molybdate, calcium acid phosphate or their mixture) was added to 200 mL of the supporting electrolyte

(0.01 M sodium chloride NaCl). A saturated calomel electrode (SCE) was used as reference. After this exposition (4 h), the morphology of the protective layer formed on the steel panel was observed by scanning electron microscopy (SEM) employing a brand microscope FEI Quanta 200 with tungsten filament. The surface elemental composition of the protective film was obtained with an energy dispersive RX micro-analyzer and the EDX detector Apollo 40. Compounds formed on the steel surface were identified by diffuse reflectance infrared Fourier transform spectroscopy analysis (DRIFTS-FTIR).

Corrosion rates were determined by the polarization resistance technique [57–59] employing the Potentiostat-Galvanostat EG & G PAR Model and a conventional three electrode cell. The working electrode was a SAE 1010 steel rod (area: 0.28 cm^2), the reference was the SCE and the counterelectrode a Pt mesh. The supporting electrolyte was similar to that employed in corrosion potential measurements but with 0.5 M NaCl. The sweep amplitude was $\pm 20 \text{ mV o.c.}$ and the scan rate 0.166 mVs^{-1} . All electrochemical measurements were carried out in normally aerated stirred solutions (300 rpm).

Polarization curves, Tafel mode, were done in a similar cell as mentioned above after 2 h of immersion in NaCl 0.5 M. In this case, the sweep amplitude was $\pm 250 \text{ mV o.c.}$ and the scan rate 1.0 mVs^{-1} .

2.1. Paints composition, preparation and application

Water-borne paints were formulated containing different amounts of calcium acid phosphate, up to 30% by volume, with respect to the total pigment content. This value is often recommended for phosphate pigments [9,10]. A similar series of paint was formulated by adding 5% of lanthanum molybdate when the calcium acid phosphate content was diminished below 30%. Titanium dioxide, barium sulphate, talc and mica were incorporated to complete the pigment formula. Mica was added due to its barrier properties and the ability to reduce “flash rusting” [60–63]. The composition of all the paints could be seen in Table 1. Paints containing 30% of calcium acid phosphate and 30% of lanthanum molybdate, respectively, were used as controls together with a paint without anticorrosion pigments.

The film forming material selected to formulate the water-borne paint was an epoxy resin, based on a mix of bisphenol A and bisphenol F. The curing agent (hardener), which also acts as emulsifier, was a modified polyamidoamine with 50% of solids. The resin/hardener ratio was 1.0/1.2 by weight. Neutral demineralised water was employed as solvent. PVC was 20% in order to produce a more impervious coating. Water-borne paint manufacture was carried out employing a high-speed disperser. Preliminary tests showed the advantage of incorporating the pigment into the hardener, instead of mixing it with the resin. Water was added firstly because of the relatively high viscosity of the hardener; then, the pigments were incorporated in accordance with their increasing oil absorption index. Mica was added at the end of the process to avoid the break-up of laminar particles.

SAE 1010 steel panels ($15.0 \times 7.5 \times 0.2 \text{ cm}$) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene and then painted by

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