

## ANTICORROSIVE WATER BORNE PAINTS WITH REDUCED PHOSPHATE CONTENT

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### INTRODUCTION

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 goal [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 solvents in paint formulations to fit VOC's regulations.

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 behaviour than chromates and better than zinc phosphate on its own.

Other anticorrosive pigments, apart from phosphates, were found to be suitable to formulate anticorrosive paints. Among them ferrites, calcium exchanged silicas, etc [26, 27]. More recently the development of intelligent anticorrosive paints was reported [28].

Non-toxic corrosion inhibitors can work synergistically with each other to give a performance greater than either one alone. In addition, other organic molecules could be used in combination with non toxic inhibitors to improve their anticorrosive performance [29].

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 [30-34]. It was stated everywhere that water-borne paints are less resistant to the corrosion process and prone to biological attack [31, 35-38]. They also exhibit "flash rusting" during solvent evaporation which finally affects the appearance of the coating [35, 38, 39].

The object of this research was to formulate water-borne coatings free of zinc and with reduced phosphate levels. Zinc phosphate was replaced by calcium acid phosphate and lanthanum molybdate was incorporated as an additive to enhance paint anticorrosive performance. Lanthanum molybdate was synthesised in the laboratory. Paints performance was assessed by accelerated tests and the electrochemical noise technique (ENM). 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.

## EXPERIMENTAL

### Pigment characterization

Lanthanum molybdate was prepared by precipitation at pH 5.5 mixing two solutions; one of the a  $2 \times 10^{-3}$  M of lanthanum nitrate and the other  $3 \times 10^{-2}$  sodium molybdate.

The corrosion potential of SAE 1010 steel electrode was monitored, as a function of time, in the corresponding pigment suspension (lanthanum molybdate, calcium acid phosphate or their mixture) in 0.01 M sodium chloride (NaCl), employing a saturated calomel electrode (SCE) as reference. The corrosion rate was also determined by the polarization resistance technique, employing a three electrode cell with a SAE 1010 steel bar as the working electrode. The electrolyte was NaCl 0,1 M and the exposure time 24 hours.

Water-borne paints were formulated containing different amounts of calcium acid phosphate. A similar series of paint was formulated but adding 5% of lanthanum molybdate and diminishing the calcium acid phosphate content. The composition of all pigment mixtures tested in this research could be seen in Table I.

**Table I. Anticorrosive Pigment composition as percentage of the total pigment content**

<b>Anticorrosive pigment</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
Lanthanum molybdate	5	5	5	---	---	30	---
Calcium acid phosphate	5	15	25	10	20	---	30

An epoxy resin, based on a mix of bisphenol A and bisphenol F, was selected to formulate the water-borne paint. 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 parts by weight. Neutral demineralized water was employed as solvent. The anticorrosive pigment content was 30% by volume with respect of the total pigment content and 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". The blank (paint 8) contained only the inert pigments. 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 x 7.5 x 0.2 cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene and then painted by brushing, up to a thickness of  $75 \pm 5$   $\mu$ m. Painted panels were kept indoors for 14 days before being tested to allow complete curing.

### The performance of anticorrosive paints through accelerated and electrochemical tests

A set of three panels was placed in the salt spray chamber (ASTM B 117) to evaluate the rusting (ASTM D 610) and the blistering (ASTM D 714) degrees, periodically, during 5350 hours. The mean value of the obtained results was reported in this paper. A similar set was placed in the humidity chamber (ASTM D 2247); and blistering and rusting degrees were evaluated, periodically, during 1180 hours.

The electrochemical assessment of painted panels was carried out with the ENM technique [40-45]. The measurement cell was constituted by two nominally identical painted panels as electrodes and a reference electrode. A low value resistor was placed between the two specimens and current noise was measured as the fluctuation in voltage across the resistor, on the grounds that interference from the electronic circuitry will be diminished [40]. The three electrodes were in the same container which made it easier to control the effect of temperature fluctuations. The edges of the specimens were blanked off leaving 37 cm<sup>2</sup> of the painted panel exposed to a 0.5M NaCl solution. Data were acquired with a NICOLET 310 digital oscilloscope and the corresponding software 310RSWFT. Adequate filtering was provided just to eliminate undesirable signals like line signals [41-43]. The sensitivity of the measuring device in the E-scale was 100μV and 100nA in current measurements. The sampling frequency was 5 Hz, which is commonly used to study corroding systems [41-43] and data were collected during 800 s. Each set of data was controlled to verify they distribute normally [5]. Statistical analysis of each time series was performed and the noise resistance (R<sub>n</sub>) was calculated as the quotient  $R_n = \sigma_E / \sigma_i$  [41-43]. Although the mean values of raw data were plotted, the d.c. trend was removed to perform R<sub>n</sub> calculation by the moving average removal procedure described by Tan et al [45].

## RESULTS AND DISCUSSION

Steel corrosion potential in the calcium acid phosphate suspension was displaced to negative values due to the formation of a phosphate layer. Lanthanum molybdate displaced steel corrosion potential to more positive values. The corrosion potential of steel in a mixture of both pigments was changed to match the corrosion potential of lanthanum molybdate (Fig. 1). Steel corrosion rate in the supporting electrolyte (NaCl 0,1M) was 14.95 μAcm<sup>-2</sup> after 24 hours of exposure. Steel corrosion rate was reduced to 4,90 μAcm<sup>-2</sup> by lanthanum molybdate and to 2.43 μAcm<sup>-2</sup> in the presence of both inhibitors.

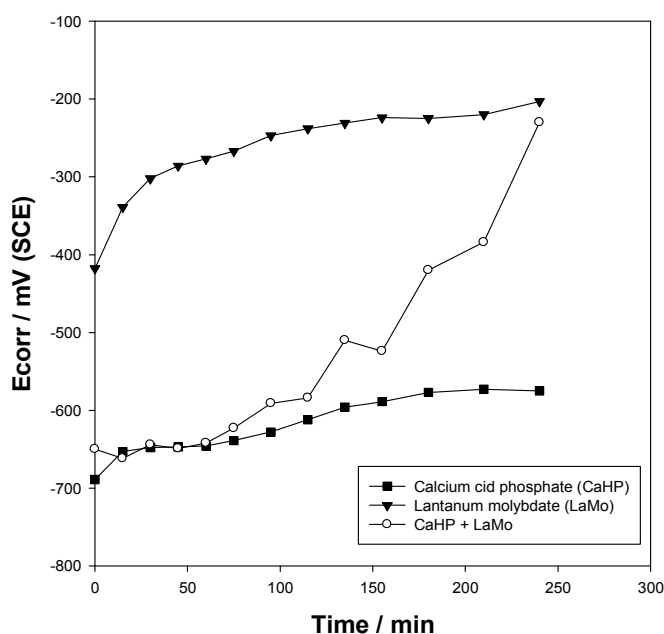


Fig. 1. Steel corrosion potential in different pigment suspensions

Results in the salt spray chamber (Table II) showed that all paints performed well after 5340 hours of exposure, except paints containing pigments mixtures 3 and 6. It could be seen that good results could be obtained with the lowest pigment contents thus reducing phosphate

loadings in paints. Blistering begun after 2570 hours and was of less magnitude for the lowest pigment contents. Blisters are smaller than in the case of the blank.

Results in the humidity chamber indicated that blistering begun after 215 hours of exposure and increased as time elapsed (Table III). In every case the presence of the anticorrosive pigments was beneficial because blisters were of smaller size than in the case of the blank. The surface density of blisters was, in every case, high, maybe due to the nature of the binder in the water-borne coating.

**Table II. Rusting (R) and blistering (B) degrees in the salt spray chamber**

PAINT	1180		1850		2570		3890		4300		5350	
	R	B	R	B	R	B	R	B	R	B	R	B
1	10	10	10	10	10	10	9	10	8	8F	8	8F
2	10	10	10	10	9	8F	8	10	8	10	8	8M
3	10	10	10	10	9	8F	7	4M	--	--	--	--
4	10	10	8	10	9	8F	8	8D	8	8F	6	8D
5	10	10	10	10	10	10	9	10	9	10	7	8MD
6	10	10	10	10	10	10	9	8F	8	8F	--	--
7	9	10	9	10	9	10	8	10	8	10	8	10
Blank	10	10	10	10	10	8M	8	8D	8	6D	6	6D

**Table III. Rusting (R) and blistering (B) degrees in the humidity chamber**

PAINT	145		215		1180	
	C	A	C	A	C	A
1	10	10	10	8D	5	6D
2	10	10	10	8D	7	6D
3	10	10	10	8D	9	6D
4	10	10	10	8D	9	6D
5	10	10	10	8D	10	6D
6	10	10	10	8D	9	6D
7	10	10	10	8D	8	6D
Blank	10	6D	10	6D	3	4D

After 140 days of immersion none of the exposed painted panels showed signs of corrosion except those corresponding to the controls. However, electrochemical activity was

detected from early times according to results presented in Figs 2 and 3. The best anticorrosive behaviour was attributed to paints with pigment formula 2 and 4, respectively, because they displaced noise potential to more positive values during at least 50 days (Fig. 2) and the coupling current was rather low during the test period. The oscillations in the coupling current were related to passivation and repassivation processes (Fig. 3). It seemed that lanthanum molybdate could improve the repassivation process, particularly at long exposure times.

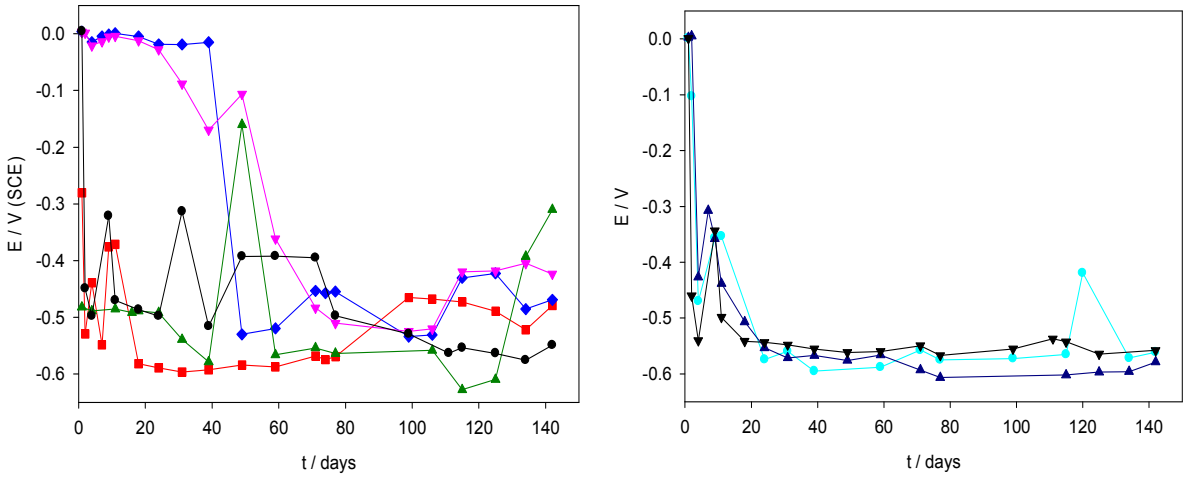


Fig. 2. Mean noise potential of steel coated with different anticorrosive paints formulated according to pigment formula in Table I

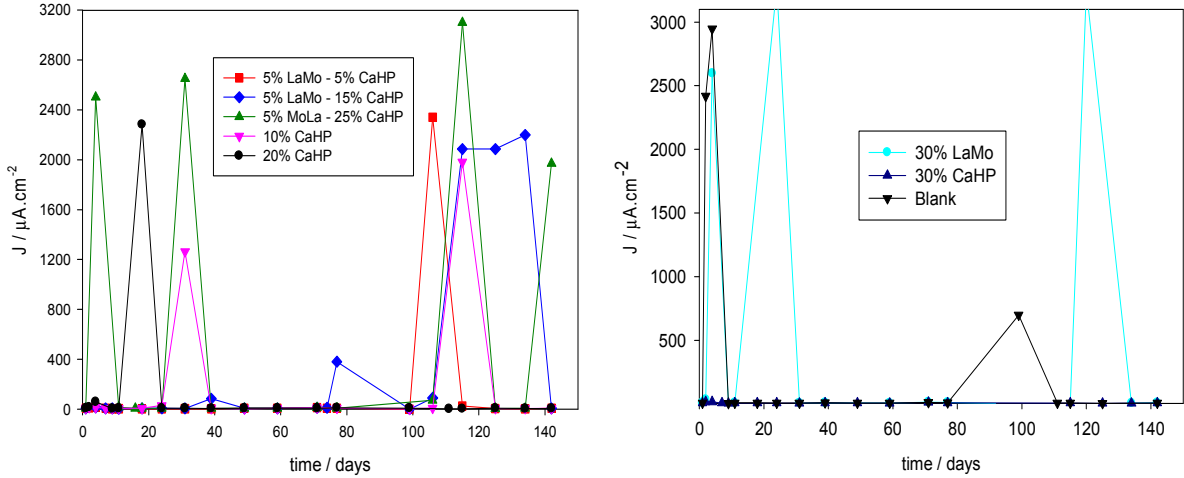


Fig. 3. Mean coupling current of steel coated with different anticorrosive paints formulated according to pigment formula in Table I

It was thought that the inhibitive properties of the pigment prevented steel from corrosion and was responsible of the low coupling currents measured in this research.

The noise resistance (Fig. 4) could be compared to the polarization resistance and it was rather low. The average value was  $\sim 2\text{k}\Omega\text{cm}^2$  and this value could be associated with the increased electrochemical active area as time went on.

## CONCLUSIONS

If correctly formulated, water-borne anticorrosive paints could afford good anticorrosive protection to steel substrates. Very good results were obtained in the salt spray chamber because several paints underwent a very long exposure time (4300) with qualifications equal or higher than 8. The replacement of zinc phosphate by calcium acid phosphate is recommended at a level of 10-20%. The incorporation of lanthanum molybdate could enhance the anticorrosive protection provided by phosphates.

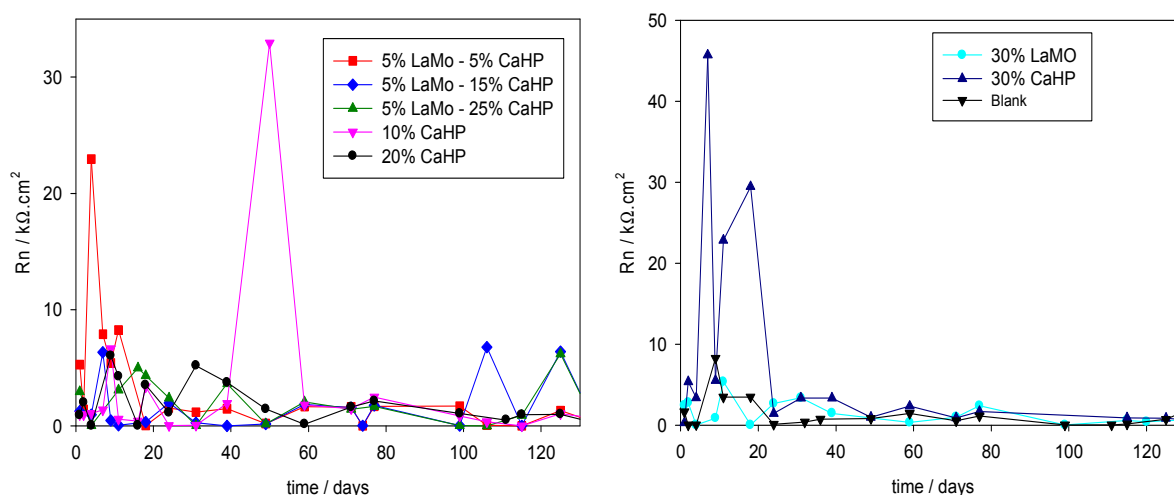


Fig. 4. Noise resistance of steel coated with different anticorrosive paints formulated according to pigment formula in Table I

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