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Ceramic microspheres to improve anticorrosive performance of phosphate paints

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Abstract

Zinc phosphate and related compounds have been proposed as ‘‘green’’ replacements for traditional anticorrosive pigments such as zinc chromate and lead oxides. However, environmental concerns have risen in the last years because the disposal of these materials in the environment increased phosphate levels in water and produce eutrophication of water bodies. The present paper deals with the possible incorporation of ceramic microspheres in alkyd paints in order to diminish phosphate content. The results suggested that paints with low phosphate content can be successfully formulated with a suitable selection of the amount and type of microspheres.

Keywords: Zinc phosphate; Ceramic microspheres; Anticorrosive paints; Barrier properties

1. Introduction

Zinc phosphate and related compounds have gained worldwide acceptance as suitable replacements for traditional anticorrosive pigments such as zinc chromate and lead oxides [1–4]. However, environmental concerns about phosphate-pigmented primers have risen because the disposal of these materials in the environment increased phosphate levels in water and produce eutrophication of water environments [5,6]. Eutrophication is a process caused by an excess of nutrients which stimulate excessive plant growth. Plants lower oxygen concentration, diminish light penetration and, as result, the biological community changes (Fig. 1). As a consequence, scientific research is focused on eliminating or, at least, diminishing phosphate content in paints.

There are two stages in the story of anticorrosive pigments for protective paints. The first one was the substitution of zinc chromates and lead oxides by zinc phosphates [1–3] and modified phosphates [7–10]. Apart from phosphates, ion exchanged silicas [11–14], spinels [15,16] and borates [17], were reported to have good anticorrosive properties. Lamellar pigments such as mica, micaceous iron oxide and aluminium leaves were also studied because they diminish film permeability to water and aggressive ions, thus restraining corrosion of the metal substrate [18–20].

The second stage was dominated by the search of ‘‘green pigments’’ designed to exhibit either intelligent behaviour or synergisms with other pigments. In this field the employment of conducting polymers (polyaniline and polypirrol) [21–25] and mixtures of pigments such as phosphate and hypophosphite [26], polyaniline with phosphates or borates [27], etc. could be found in the literature.

The present work studied the incorporation of two different silica-alumina-ceramic-spheres to paints in order to lower the zinc phosphate content without impairing their anticorrosive properties. These aluminosilicates were characterized by current analytical techniques and their protective properties by electrochemical tests (corrosion potential and linear polarization measurements). Solvent borne paints were formulated employing an alkyd resin as film forming material. Steel panels were painted and, then, tested in the salt spray cabinet and the humidity chamber. Paints anticorrosive performance was also assessed by electrochemical tests such as corrosion potential and ionic resistance measurements. Results showed that the main action of the microspheres was to enhance the barrier properties of the coating in such a way that zinc phosphate content can be diminished sensibly.

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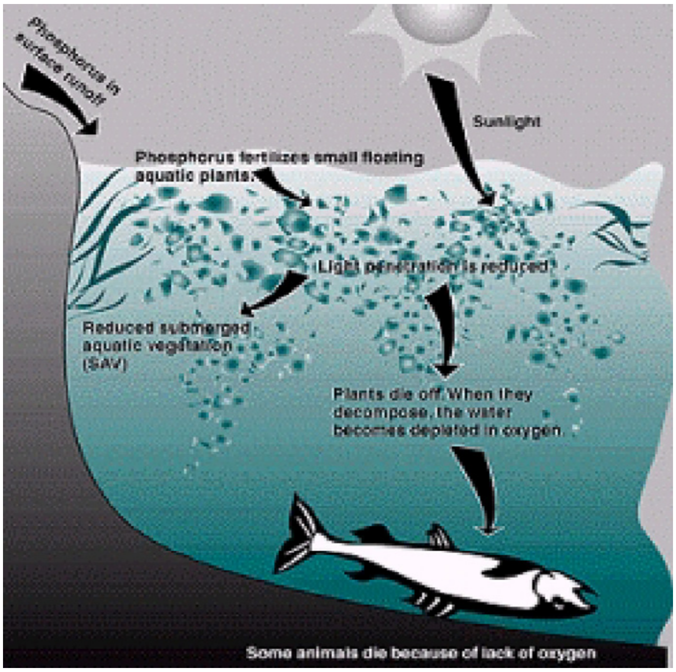

Fig. 1. Biological effects of eutrophicacion. From ''Phosphate removal: a novel approach'', J.W. Mc Grath and J.P. Quinn.

2. Materials and methods

2.1. Pigments characterization

Two different ceramic microspheres (G and W) were selected to carry out this research. Their characteristics may be found in the corresponding technical sheet [28,29]

The composition of the aluminosilicate microspheres was obtained by current analytical techniques. Their physico-chemical properties relevant to paint technology, such as density and oil absorption, were determined according to standarized procedures (ASTM D 1475 and ASTM D 281, respectively). The size of the spheres was determined with a Malvern Particle Analyzer and their shape was observed by Scanning Electron Microscopy (SEM). pH, conductivity and soluble salts content of their water extracts were also determined.

Electrochemical essays were done in order to ensure that ceramic spheres do not influence steel corrosion. Corrosion potential of SAE 1010 steel electrodes immersed in a suspension of the spheres in 0.025 M NaCl was measured as a function of time, employing a saturated calomel electrode (SCE) as reference.

Steel corrosion rate in G and W pigments suspensions, in 0.1 M NaCl, was obtained from polarization curves employing Tafel's approximation. A SCE and a platinum grid were used as reference and counterelectrode, respectively. The swept amplitude was ±0.250 V from the open circuit potential and the scan rate 0.5 mV s^{-1}. Measurements were carried out with a Potentiostat/Galvanostat EG&G PAR Model 273 A plus SOFTCORR 352 software.

2.2. Formulation, elaboration and application of paints

A medium oil alkyd resin (50% linseed oil, 30% o-phtalic anhydride, 8% pentaerythritol and glycerol and 12% pentaerythritol resinate) was employed as the film-forming material and white spirit as the solvent. The pigment volume concentration/critical pigment volume concentration (PVC/CPVC) relationship was 0.8. It should be pointed out that a solvent borne alkyd resin was chosen because its behaviour has been well documented for many years.

Paints were formulated with different ceramic spheres/barium sulphate ratios (100/0, 70/30, 50/50, by volume, v/v). The anticorrosive pigment was zinc phosphate (10%, v/v respect to the total pigment content) while titanium dioxide and zinc oxide were the complementary pigments.

Two control paints were formulated: one of them with 10% (v/v) of zinc phosphate, the other with 30% (v/v). This last content was recommended in the specialized literature to achieve good anticorrosive performance while a poor behaviour was observed with 10% of zinc phosphate [4]. Pigment compositions are shown in Table 1.

All pigments were dispersed for 24 h in the vehicle (resin plus solvent), employing a ball mill, to achieve an acceptable dispersion degree.

SAE 1010 steel panels (15.0 cm × 7.5 cm × 0.2 cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene and, then, painted by brush, to reach a dry film thickness of 70 ± 5 μm. Painted panels were kept indoors for 14 days before testing.

From now on, paints will be named with the letter corresponding to the type of sphere employed in the formulation (G or W) and with a number, corresponding to the pigment formulation (1, 2 or 3) displayed in Table 1. Paints

Table 1
Pigment composition of paints as percentage by volume of solids.

Components	Paints				
	1	2	3	4	5
G or W	35.4	25.3	17.7	–	–
Zinc phosphate	10.0	10.0	10.0	10.0	30.0
Titanium dioxide	19.2	19.2	19.2	19.2	11.9
Zinc oxide	35.4	35.4	35.4	35.4	29.1
Barium sulphate	0.0	10.1	17.7	35.4	29.1
G or W/Barium sulphate ratio	100/0	70/30	50/50	0/100	0/100