Available online at www.sciencedirect.com
SCIENCE DIRECT®
Applied Surface Science 252 (2005) 1386–1397
applied surface science
www.elsevier.com/locate/apsusc

Three generations of inorganic phosphates in solvent and water-borne paints: A synergism case

G. Blustein, M.C. Deyá, R. Romagnoli *, B. del Amo

CIDEPINT–Centro de Investigación y Desarrollo en Tecnología de Pinturas, Laboratorio de Estudios Electroquímicos Aplicados, (CIC-CONICET), Calle 52e/121 y 122, (B1900AYB) La Plata, Argentina

Received 2 February 2005; received in revised form 17 February 2005; accepted 17 February 2005
Available online 1 April 2005

Abstract

This research work is intended to compare the anti-corrosive properties of three generations of inorganic phosphate pigments in solvent-based paints and in water-borne ones, both of the epoxy type. The anti-corrosive properties of phosphate pigments were assessed by means of electrochemical techniques (corrosion potential measurements, polarisation tests, etc.), employing a steel electrode dipped into pigments suspensions. The behaviour of these pigments in anti-corrosive paints, formulated with different binders, have been studied by accelerated (salt spray cabinet and humidity chamber) and electrochemical tests (corrosion potential and ionic resistance measurements).

Accelerated and electrochemical tests allowed to differentiate the anti-corrosive performance of the three phosphates studied in this research. These test are also able to detect and characterise possible synergism between the water-borne resin and the pigments.

Keywords: Corrosion protection; Steel passivation; Coatings; Phosphate pigments; Synergism; Protective layer

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 anti-corrosive 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 modifica-

* Corresponding author. Tel.: +54 221 4831141/44; fax: +54 221 4271537.
E-mail address: estelectro@cidepint.gov.ar (R. Romagnoli).

0169-4332/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2005.02.096

tions 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].

As a general rule, it can be said that the protective action of phosphates is due to the formation of an iron oxyhydroxides film, on the steel substrate, which is non expansive in nature. It also involves the polarisation of cathodic areas by the precipitation of sparingly soluble salts which adhere to the surface [2,26,27].

Due to the imposition of the increased legislative restrictions on the emission of the organic materials to the atmosphere, water-borne coatings are finding more and more importance for both do-it-yourself and industrial coatings applications. Water, as a solvent, has two main advantages because it is non-toxic and non-flammable. Water-borne systems present a range of characteristic differences and, in some cases, difficulties not exhibited by solvent-borne paints [28–32]. It was stated everywhere that water-borne paints are less resistant to the corrosion process generated by water, ions and oxygen permeation and prone to biological attack [29,33–36]. They also exhibit ''flash rusting'' during solvent evaporation which finally affects the appearance of the coating [33,36,37].

The objective of this research was to compare the anticorrosive performance of solvent and water-borne paints, formulated with three anti-corrosive pigments, belonging each one to a different generation of phosphate pigments. The anti-corrosive behaviour of the paints was evaluated through accelerated and electrochemical tests.

2. Experimental

2.1. Pigment characterisation

Three different pigments were selected to carry out this research: zinc phosphate (Pigment 1), zinc molybdenum phosphate (Pigment 2) and zinc tripolyphosphate (Pigment 3). The two former pigments were commercially available; the last one was prepared in the laboratory, by precipitation from the corresponding soluble salts [25].

Pigments composition was established employing current analytical techniques. Physicochemical properties of pigments, relevant to paint technology, such as density (ASTM D 1475) and oil absorption (ASTM D 281), were measured, according to standardised procedures, in order to sketch a correct formulation of the paint. The pH and the ionic composition of the aqueous saturated solution were also determined.

The inhibitive properties of the anticorrosive pigments were evaluated by means of electrochemical techniques, employing SAE 1010 steel electrodes with low surface roughness (mean peak-to-valley height 1.40 μm), in pigments suspensions. The corrosion potential was monitored as a function of time, in the corresponding pigment suspension, against a saturated calomel electrode (SCE) as reference and 0.025 M sodium perchlorate as supporting electrolyte.

Steel corrosion rates, in pigments suspensions in 0.5 M sodium perchlorate, were obtained from polarisation resistance measurements. A SCE and a platinum grid were used as reference and counter electrodes, respectively. The swept amplitude was ±20 mV from the open circuit potential and the scan rate 0.250 mV s^{-1}. Measurements were carried out with a Potentiostat/Galvanostat EG&G PAR Model 273A plus SOFTCORR 352 software. Anodic and cathodic polarisation curves, in a wider potential range, were also obtained employing a similar electrolytic cell. The electrochemical experiments were repeated adding to the electrolyte solution the resin and the hardener used to formulate the water-borne paints. These two components were dosed in the same proportion as in the paint (resin/hardener ratio: 1.0/1.2 parts by weight).

2.2. Paints composition, manufacture and application

Two different epoxy paints were formulated to carry out this research; one of them was a solvent-borne paint and the other a water-borne one.

The resin employed to formulate solvent-borne paints was a bisphenol epoxy-polyamide resin (1:1 ratio v/v). The corresponding solvent mixture was composed of xylene/methyl isobutyl ketone/butyl cellosolve (13/45/42%, by weight). The PVC/CPVC relationship was 0.8 as suggested elsewhere [9,10]. The anticorrosive pigment load was 30% v/v of the total pigment content; as suggested in the literature for phosphate pigments [6,9,10]. Titanium dioxide, barium sulphate and talc complete the pigment