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Study of zinc tannates prepared with Tara powder (*Caesalpinia spinosa*) as anticorrosive pigments in alkyd paints and wash primer formulations

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ABSTRACT

The aim of this research was to evaluate the anticorrosive properties of alkyd paints and wash primers formulated with zinc tannates containing Tara tannins. Their inhibitory efficiency was compared with paints pigmented with well-known anticorrosive pigments by accelerated corrosion tests (salt spray test, Prohesion test, and sulphur dioxide test), natural exposure tests and some electrochemical techniques (corrosion potential, polarization resistance and impedance measurements). It was demonstrated that the capacity of inhibiting corrosion of zinc tannates is equivalent to that shown by most commercially available conventional pigments, such as zinc phosphate and zinc chromate.

1. Introduction

The use of organic coatings is the most commonly employed method to protect metal structures against corrosion [1–7]. Anticorrosive pigments are dispersed homogeneously throughout the paint film in order to enhance protection by any of these three main mechanisms: barrier effect, cathodic protection and inhibitory effect [6,8–10]. The commercial value of all anticorrosive pigments is calculated with certain quality parameters: level of toxicity, inhibiting efficiency and price [11].

Nowadays, the paint industry is in search of environmentally friendly pigments that could substitute the widely used conventional anticorrosive pigments [3,4,10–13], such as lead or chromate, because of their harmful toxicity [14–16]. Even at present, the use of phosphates, pigments with an equivalent anticorrosion behaviour [1–5,8,13,17–20] with a lesser level of toxicity [21], has increased the environmental concern, because they cause eutrophication of freshwater reserves [22].

Paint trends are constantly changing as health and safety legislations multiply. Although phosphate pigments dominate the market [23], other inhibitory compounds are being developed [22–27]. Metal tannates, compounds containing tannins, have received special attention in recent years [27–34]. Vegetal tannins are non-toxic, biodegradable organic compounds that can be obtained at reduced costs [35]. Tannic acid can act as a ligand, forming soluble or insoluble complexes with several metals, etc. [36,37]. Tannins are distributed in two groups according to their structure: hydrolysable and condensed. The use of hydrolysable tannins has been limited; only few researches have been published in the field of antifouling paints [28,29,32] and rust converters [38–41]. However, it has been shown that tannins could improve the corrosion behaviour of a coating system [42,43].

The aim of this research is to validate the use of zinc tannates prepared with Tara (*Caesalpinia spinosa*) hydrolysable tannins as anticorrosive pigments in alkyd paints and wash primer formulations, in order to study their inhibitory efficiency. The low cost, high ease of application and good adhesion of alkyd-base coatings have turned them into the most important and widely applied protection method against corrosion [44–46], specifically in moderate corrosive environments [46]. Meanwhile, wash primers are reported as traditional formulations prepared with a polyvinylbutiral resin, an anticorrosive pigment and phosphoric acid [47–49]. These pre-treatment coatings are responsible for preventing or retarding the spread of corrosion until the topcoat is applied, and effectively act as a tie-coat, improving the adhesion of the subsequent coat with the metal substrate [47,48].

Accelerated corrosion tests (salt spray test, Prohesion test, and sulphur dioxide test), natural exposure tests and electrochemical tests (corrosion potential and polarization resistance measurements) were performed to assess the corrosion protection properties of paints pigmented with zinc tannates. For comparative studies, paints containing conventional pigments (zinc chromate and zinc modified phosphate) were prepared and evaluated in parallel.

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2. Experimental

2.1. Materials and films preparation

2.1.1. Pigments

Zinc tannates prepared with Tara powder and zinc oxide were used to manufacture alkyd paints and wash primers. Tara powder was obtained from SILVATEAM Peru (Callao, Peru). Zinc oxide (ZnO) was purchased from Industrias Electroquímicas S.A. (Callao, Peru). Yellow zinc chromate and a zinc phosphate modified with molybdenum were also employed as commercial well-known anticorrosive pigments for comparison purposes.

2.1.2. Paints manufacture and application

Paints were formulated employing high-speed disperser equipment. Pigment concentration was changed according to the volume of zinc chromate used to ensure the same pigment volume concentration (PVC) in all formulations. All pigments were incorporated in accordance with their increasing oil absorption. In all cases, paints were applied using a spray gun (2 coats). Environmental conditions were controlled during application.

In all cases, the average dry film thickness was measured with a Deltascope MP30 equipment, brand Fischer (Tables 1 and 2). The edges of the coated panels were protected with a grey, waterproof polyethylene tape (Brand 3M, model 3939). According to ASTM D1654-05 standard, a linear incision was applied to one of the plates of each paint/painting system, at the bottom of the specimen with a scribing tool (brand Erichsen).

2.1.3. Wash primers

Four types of two-pack wash primers (WP) were prepared with the following anticorrosive pigments: zinc chromate (WCr), zinc phosphate modified with zinc molybdate (WF), zinc tannate TZn3 (WTZ3) and zinc tannate TZn4 (WTZ4). The weight percentages of the components used in the formulation of the wash primer are shown in Table 3. Both fractions, part A and part B, were mixed in a 4–1 ratio, before paint application.

For accelerated and natural exposure tests, panels (JIS G3141, SPCC grade) of 10 cm x 15 cm were previously polished using a grinder with an emery paper No. 100, and then polished manually in two directions with emery paper No. 100. They were finally degreased with ethanol and then coated. The composition of JIS G3141 mild steel is as follows: C: 0.15%, Mn: 0.60%, S: 0.05% and P: 0.10%.

Four specimens were painted for each type of wash primer. Two coated panels were selected to apply a top layer of synthetic, white, commercial alkyd paint, and were identified with a letter S at the end of its name (e.g., WP-S). The mean value of the dry film thicknesses is reported.

For electrochemical measurements, JIS G3141 (2 cm x 6 cm x 3 mm) mild steel panels, were abraded with No 100 emery paper, degreased with ethanol, and finally coated. A square zone of 1 cm^2 was delimited with paraffin to use as working electrodes.

2.1.4. Alkyd paints

Four types of alkyd paints (AP) were prepared with the following anticorrosive pigments: yellow zinc chromate (ACr), zinc phosphate modified with zinc molybdate (AF), zinc tannate TZn3 (ATZ3) and zinc tannate TZn4 (ATZ4). The weight percentages of the components used in the formulation of alkyd paints are shown in Table 4.

Test panels (JIS G3141, SPCC grade) of 10 cm x 15 cm were sandblasted, meeting the requirements of the standard ASTM D4940. An average roughness of 2.3 mils was attained. Panels were cleaned up and then coated.

For the accelerated tests, salt spray test and Prohesion test, as well as for the natural exposure tests, six specimens were painted for each type of alkyd primer. A top layer of synthetic, white, commercial alkyd paint, was applied to half of the samples and were identified with a letter S (e.g., AP-S). For the SO_2 salt fog test only two coated panels with each type of primer, alone and in a paint system, were tested. The mean value of the dry film thicknesses is reported.

2.2. Characterization of zinc tannates

The Fourier spectrums of zinc tannates and Tara powder were obtained using the potassium bromide disc technique and a Perkin–Elmer Spectrum 100 FTIR Spectrometer. The following physicochemical properties were analysed according to international standards: Oil Absorption by Spatula Rub-Out (ASTM D281), pH of aqueous extract (ISO 787/9), specific gravity (based on ASTM D153), residue on sieve (based on ASTM D185), matter solubility in water at 25 °C (ISO 787/8) and ≥100 °C (ISO 787/3), and loss of ignition (ISO 6745/7).

Filtrated suspensions prepared to determine matter solubility in water at different temperatures (ISO 787/8 and ISO 787/3) were used to calculate the amount of soluble chlorides and sulphates in metal tannates by EPA Method 300.0. A LaChrom Merck-Hitachi ion exchange chromatography equipment coupled with a LaChrom L-7470 Merck-Hitachi detector was employed. To analyse the amount of zinc in the synthesized tannates, the preparation of the test solutions was carried out in accordance with the standard test method ISO 6745/8, and the content of zinc in aqueous solutions was quantified with a OPTIMA

Table 1
Dry film thicknesses of mild steel specimens painted with wash primers and alkyd paints used in accelerated corrosion tests.

Sample	Salt spray test		Prohesion test		SO_2 test	
	Primer (μm)	System (μm)	Primer (μm)	System (μm)	Primer (μm)	System (μm)
WCr	16.8	–	14.5	–	–	–
WF	20.4	–	21.6	–	–	–
WTZ3	17.0	–	19.1	–	–	–
WTZ4	18.2	–	18.7	–	–	–
WCr-S	16.1	48.1	13.0	46.7	–	–
WF-S	13.7	39.8	17.8	53.7	–	–
WTZ3-S	13.9	54.9	15.5	52.6	–	–
WTZ4-S	15.2	50.5	15.7	53.8	–	–
ACr	40.9	–	29.5	–	31.4	–
AF	40.6	–	43.7	–	48.5	–
ATZ3	40.6	–	30.9	–	31.9	–
ATZ4	41.2	–	44.5	–	28.4	–
ACr-S	24.7	71.6	15.8	67.6	19.1	67.6
AF-S	21.9	71.9	33.1	85.8	32.8	82.5
ATZ3-S	24.9	79.1	27.3	76.7	30.3	74.6
ATZ4-S	22.7	72.5	37.5	85.6	35.9	84.6