



Zinc tannate and magnesium tannate as anticorrosion pigments in epoxy paint formulations



Ariane V. Zmozinski^{a,*}, Rafael S. Peres^b, Kelly Freiberger^{b,c}, Carlos A. Ferreira^c,
Silvia Margonei Mesquita Tamborim^a, Denise S. Azambuja^a

^a Instituto de Química, Universidade Federal do Rio Grande do Sul, 91501-970, Porto Alegre, RS, Brazil

^b Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul – IFRS, 95770-000, Campus Feliz, Rua Princesa Isabel, 60, Bairro Vila Rica, Feliz, RS, Brazil

^c LAPOL/PPGE3 M – Laboratório de Materiais Poliméricos, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970, Porto Alegre, RS, Brazil

ARTICLE INFO

Keywords:

Black wattle tannin
Corrosion
Zinc tannate
Magnesium tannate
Organic coatings

ABSTRACT

Vegetable tannins are natural, non-toxic, water-soluble polyphenols present in the roots, branches, leaves, flowers, fruits, and seeds of various trees. Tannins can remove rust and inhibit corrosion. Because the high solubility of tannins in water may impair their use as an anticorrosion pigment, a reduction in solubility is necessary. In this work, two tannin-based anticorrosive pigments were synthesized by the reaction of black wattle tannin with zinc and magnesium salts to form zinc tannate and magnesium tannate, respectively. Pigment synthesis was verified by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). Epoxy coatings containing both tannates were formulated and their corrosion performance was evaluated using electrochemical impedance spectroscopy (EIS) and salt spray tests. Corrosion tests showed that zinc tannate was an excellent anticorrosive pigment in neutral saline media making it an environmentally friendly option for anticorrosive coatings.

1. Introduction

Corrosion protection refers to optimization of factors that prevent corrosion, mainly through use of protective paints. However, it was only in the nineteenth century that corrosion was recognized as a problem of great economic significance [1]. Anticorrosive paint is a mixture of insoluble particles called pigments in an organic or aqueous continuous vehicle called a resin or matrix [2]. The pigments must have anticorrosive properties so that the coating protects against corrosion [2]. Due to the high toxicity of many anticorrosive pigments, green alternatives have been developed in recent years [3,4].

Naderi and Attar [3] proposed use of strontium aluminium polyphosphate as an anticorrosive pigment for an epoxy coating. Darvish et al. [5] reported better performance of zinc aluminium phosphate than conventional zinc phosphating. Sanaei et al. [6] developed an anticorrosive pigment with a zinc acetate-cichorium complex that had excellent anticorrosive properties. Wahba et al. [7] tested complexes derived from methoxy-tolidine and salicylaldehyde against corrosion.

Tannins are polyphenolic substances used in the defence mechanisms of plants and for tanning animal hides [8,9]. These compounds have been used for more than four decades in boiler feed-water and water cooling systems to prevent corrosion of internal parts of these

equipment [10,11]. Tannins are highly soluble in water, but their metallic complexes have limited solubility when synthesized in the presence of oxygen [12]. An insoluble ferric complex acts as a barrier against oxygen diffusion, but it is not formed in strongly acidic media [13,14]. Thus, tannins are responsible for reducing the oxygen concentration in aerated aqueous medium and producing a protective film [10]. Jaén et al. [15] attribute the inhibitory action mechanism of tannins to the transformation of iron corrosion products (lepidocrocite and goethite) into inert and stable products. The transformation of lepidocrocite (γ -FeOOH) to magnetite (Fe_3O_4) in the presence of mimosa tannin was also reported by Ross et al. [16].

According to Martinez et al. [13,14], tannins can act as corrosion inhibitors due to the physical or chemical adsorption. At low pH values, chemical adsorption occurs through the free pair of electrons (from the OH^- group present in the polyphenols) and the metal surface [13]. The adsorption free energy values suggest the mechanism of physical adsorption at high pH values [13]. Dargahi et al. [11] confirmed the efficiency of a tannin blend as corrosion inhibitor for mild carbon steel in alkaline medium. Rahim et al. [17] described a reduction in the inhibition efficiency of mangrove tannin with increasing alkalinity of the medium. Different studies have shown the applicability of the pure tannins as corrosion inhibitors [11,13,14,16–20]. However, their direct

* Corresponding author.

E-mail address: arianezmozinski@gmail.com (A.V. Zmozinski).

application as anticorrosion pigments is challenging due to their water solubility. Some authors have reported the use of tannin solutions in waterborne primers [21,22].

Addition of complexing metals such as zinc and magnesium to tannins may improve their anticorrosive properties. These complexes can also decrease the solubility of tannins in water, improving their anticorrosive properties. The goal of this study is to verify the efficiency of two tannin complexes as anticorrosive pigments: zinc tannate and magnesium tannate. Both pigments have a low metals content and are environmentally friendly, using tannins obtained from the black wattle tree. Epoxy coatings containing the synthesized pigments were prepared and tested in neutral and acidic saline environments.

2. Experimental

2.1. Materials

All solutions and samples were prepared with analytical grade reagents. To prepare the tannate pigments, $Zn(NO_3)_2 \cdot 6H_2O$ (synth, Brazil) powder, Mg_2SO_4 (Vetec, Brazil) powder, HCl (Vetec, Brazil), NaOH (Synth, Brazil) and black wattle tannin (Tanac, Brazil) were used. NaCl (synth, Brazil) and HCl (Vetec, Brazil) were used for preparation of electrolyte solutions. Araldite® GZ 7071 × 75 (Huntsman, USA) epoxy resin and Aradur® 450 (Huntsman, USA) curing agent were used as a matrix for preparation of coatings. TiO_2 (Polimerum, Brazil) was used as a pigment for coating preparation. Carbon steel samples (0.108% C, 0.42% Mn, 0.12% Cr, 0.053% S, and 0.016% P) were used in all tests.

2.2. Preparation of anticorrosive pigments

2.2.1. Zinc tannate

First, 20 g of black wattle tannin were weighed in a Becker and dissolved in 1000 mL of deionized water. After dissolution of the tannin, 20 mL of a 1 M $Zn(NO_3)_2 \cdot 6H_2O$ solution was added. The pH was then adjusted to 7.5 with a NaOH solution and the mixture was stirred for 1 h [23]. After stirring, the solution was filtered and dried at 110 °C for 6 h.

2.2.2. Magnesium tannate

First, 20 g of black wattle tannin were weighed in a Becker and dissolved in 1000 mL of deionized water. After dissolution of the tannin, 40 mL of a 1 M $MgSO_4$ solution was added. The pH was then adjusted to 8.0 with a 0.5 M NaOH solution and the mixture was stirred for 1 h. After stirring, the solution was filtered and dried at 110 °C for 6 h.

The zinc and magnesium tannates were milled and sieved in a 20 µm sieve before coating dispersion. The particle size of both pigments was between 6 and 7 Hegman (25 µm and 13 µm), measured with a grind gauge (BYK, Germany). According to the particle size distribution (Tegape sieves, Brazil), the mean particle size for zinc tannate pigment was 18 µm and for magnesium tannate was 16 µm. There are no significant morphological differences between the two pigments.

2.3. Pigment characterization

The zinc and magnesium tannates were characterized by TGA, and FTIR. The FTIR spectrum was measured using a Perkin Elmer Spectrum 1000 spectrometer with KBr pellets. TGA (TA Instruments TGA 2050) analyses were performed with approximately 20 mg of sample heated at 20 °C/min in a nitrogen atmosphere.

2.4. Coating and sample preparation

The epoxy resin was added in the jacketed reactor of a Dispermat N1 (VMA-Getzmann GmbH of Reichshof, Germany) disperser equipped with a Cowles disk and stirred for 15 min. The solid pigments were then

Table 1
Coatings composition.

Sample	Abbreviation	Components	Mass (%)	PVC (%)
Blank	BL	Epoxy resin	43.0	25
		Curing Agent	9.0	
		TiO_2	48.0	
Zinc Tannate Coating	ZnT	Epoxy resin	56.0	25
		Curing Agent	12.4	
		Zinc Tannate	29.0	
		TiO_2	2.6	
Magnesium Tannate Coating	MgT	Epoxy resin	56.0	25
		Curing Agent	12.4	
		Magnesium Tannate	29.0	
		TiO_2	2.6	
		TiO_2	2.6	

added and the mixture was kept in the disperser for 1 h. Coating compositions and pigment volume concentrations (PVC) are given in Table 1. PVC values were kept constant to allow comparison between anticorrosive pigments.

After the coating preparation, steel samples were degreased with acetone, polished with #150 sandpaper, and degreased again. The curing agent was then mixed with the coatings and the steel samples were brushed with the paints.

2.5. Corrosion experiments

Electrochemical impedance spectroscopy (EIS) was carried out using an AUTOLAB PGSTAT 302N potentiostat coupled to a frequency response analyser. All measurements were performed in potentiostatic mode at the open circuit potential with an amplitude of 10 mV and frequencies ranging from 100 kHz to 10 mHz. The working electrode (coating) size was delimited by an electrochemical cell (4 cm²). A saturated calomel electrode (SCE) was used as a reference electrode and a platinum wire (spiral geometry) was used as an auxiliary electrode. The electrolyte used in the EIS measurements was 3.5% NaCl (w/v). In the acidic medium experiments, the pH of the 3.5% NaCl (w/v) solution was adjusted to 2. Coating thicknesses for EIS experiments were: 142 ± 10 µm for MgT, 148 ± 13 µm for ZnT, and 141 ± 11 µm for BL.

Salt spray tests were performed according to the standard ASTM B117 [24] and ASTM D714 [25]. A central cut was made in all coatings to determine electrolyte migration. The dry paint film thickness was measured with a Byko-test 7500 electromagnetic film thickness gauge (BYK Gardner, Germany). The mean value of six different areas of the steel samples was used to calculate the final dry film thickness. Steel samples (50 mm × 50 mm) were painted with BL, ZnT, and MgT coatings until reaching a thickness of: 134 ± 7 µm for MgT, 131 ± 13 µm for ZnT, and 135 ± 6 µm for BL.

2.6. Coating characterization

Adhesion measurements were made according to the ASTM D3359 standard test [26]. Orthogonal cuts (1 mm) were made over the coatings. The surface was cleaned and Scotch-880 (3M, USA) tape was attached over the cuts. The tape was pulled off at an angle close to 180° in relation to the coating plane. The detached area (without coating) was used to measure the degree of adhesion. The coatings adhesion was also measured with a PosiTest® AT-A pull-off adhesion tester (DeFelsko, USA). Dollies (14 mm diameter) were glued over the coatings (six replicates) and pulled off the surface. Coating adhesion was measured in MPa using a pull rate of 0.25 MPa s⁻¹. Tests were in accordance with ASTM 4541 [27].

Optical microscopy images were obtained by a Dino-lite model AD7013MT USB digital microscope.

Download English Version:

<https://daneshyari.com/en/article/7105602>

Download Persian Version:

<https://daneshyari.com/article/7105602>

[Daneshyari.com](https://daneshyari.com)