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Accelerated Corrosion tests of epoxy-based coatings containing zinc tannates

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Abstract

Accelerated corrosion tests were performed to evaluate the efficiency of epoxy paints (primers) prepared with different anticorrosive pigments to protect structural steel. Nowadays, sustainable technology goals in the paint industry seek to replace the widely used conventional anticorrosive pigments, such as lead or chromate, because of their harmful toxicity to the environment and human health. Previous studies on alkyd coatings have shown that zinc tannates prepared with Tara tannins have the necessary requirements to be considered an efficiently, green and low-cost alternative for prevention of corrosion. Results showed that epoxy primers formulated with zinc tannates exhibited an equivalent anticorrosive behavior to phosphate base coatings and an equivalent or superior performance to those prepared with zinc chromate after salt spray (3500 h) and sulfur dioxide (2500 h) accelerated tests.

Keywords: accelerated corrosion test, coating, epoxy, steel, tannate

Introduction

Epoxy coatings have been widely used on steel substrates to protect them against corrosion due to their high cross-linking density and strength adhesion [1,2]. They have found widespread usage in the coating industry, because of their excellence resistance to heat, water, and chemicals, high stability after curing process, etc. [3,4]. Nevertheless, the major drawback of these coatings is that in the cured state, they have poor ultraviolet radiation resistance, which produced yellowing and chalking [3,5]. For this last reason, epoxy coatings are limited to maintenance work, as well as primer and intermediate coatings [3].

The primer is an essential component for corrosion protection [6]. It provides adhesion of the coating to the substrate and gives to metallic substrates reliable protection against oxidation, since it is primarily composed of inhibitory pigments [6,7]. The toxicity, inhibitive efficiency and price of a commercial anticorrosive pigment determine its quality [8]. Through the years, classical inhibitors based on hexavalent chromium and lead compounds have been used in anticorrosive coating [3,9]. The use of other inorganic compounds as corrosion inhibitor pigments has been studied; like zinc phosphate derivatives [7]. However, sometimes their efficiency does not exceed that of chromates [9]. Though, the paint industry is still in search of new ecological pigments, as a result of worldwide concerns and regulations that delimit or restrict the use of chromates.

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In recent years, the ease of tannins to form complexes with several metals has increased its use as raw materials for the synthesis of pigments, known as metal tannates. It has been proved that metal tannates from hydrolysable tannins can impart antifouling properties [10–12], act as rust converters [13–16], or improve the corrosion behavior of a coating system [17–21]. The aim of this study, based on M. Gonzales (2019) work [22], is to evaluate the inhibitory efficiency of epoxy primers pigmented with zinc tannates (hydrolysable tannins) and compare their performance with well-known anticorrosive pigments by accelerated corrosion tests.

Methodology

For the primer manufacturing, a solvent-borne epoxy resin KER 3001-X-75 (Kumho P&B Chemicals, Korea) was used. Zinc tannates (T3 and T4) prepared with Tara tannins (characterized in our previous work [19]) and commercial yellow zinc chromate and a zinc phosphate modified with molybdenum were used as anticorrosive pigments. The paint formulation process was carried out based on J. Chuman (2017) work [21]. The same pigment volume concentration (PVC) was used in all formulations. Epoxy resins were applied by brush over mild steel panels (JIS G3141). A polyamide hardener (curing agent) was used in a 3:1 mix ratio. The paint/catalyst mixtures were allowed to react in the pot (induct) for 15 minutes before they were applied.

For the accelerated tests, salt spray test (ASTM B-117) and sulfur dioxide test (ASTM G87, method B), six specimens were painted for each type of epoxy primer. A layer of commercial epoxy paint finish was applied to half of each group's plates; those samples were identified with a letter *S*. Each layer was allowed to dry one week. A linear incision was applied to one of the plates of each primer/painting system. The degree of rusting (ASTM D610), degree of blistering (ASTM D714) and degree of failure near the incision (ASTM D1654) were evaluated.

Results and discussion

After 3500 h in the salt spray test, chromate-based primers exhibited the worst performance over time, developing the highest level of oxidation (8S) and blistering frequency (4MD) at the end of the test. Their lower performance might be related with the wide range of solubility of zinc chromates, between < 0.01 % and 0.1 % [23]. Regarding the degree of rusting, EP-T3 (9P) and EP-T4 (9S) primers had a similar anticorrosive behavior than EP-Ph primers (9P). However, few blisters were developed in EP-T3 (4F) and EP-T4 (2F) primers. In the case of EP-T3 epoxy paints, formed oxide dots began to change from reddish brown to black from the second week of trial. This behavior has been attributed to the formation of iron tannates, insoluble sub-products that inhibit rust proliferation [16, 19].

Epoxy systems, primer with commercial epoxy top coat, showed no signs of oxidation after 3500 hours of testing. Nevertheless, the blistering tendency for epoxy systems was similar to that observed for primers alone: EP-Cr-S, 4M > EP-T3-S and EP-T4-S, 2F > EP-Ph-S, 10. The epoxy system with EP-Cr primer developed blisters after 1008 h of exposure (4F), increasing their blistering frequency at the end of the test (up to 4M). Blisters were not formed in systems containing phosphate based primers. On the other hand, blisters started to appear in epoxy systems with primers containing T3 (2F) and T4 (2F) tannates, after 14 and 16 weeks of testing, respectively. All epoxy primers and systems had high adhesions near the incision lines, as only paint traces were removed after scraping (EP-Ph-S, No.10 > EP-Cr-S - EP-T3-S - EP-T4-S, No.9).

In the sulphur dioxide chamber test, although primers EP-Ph and EP-T4 showed signs of oxidation after 24 h of testing (9P), and EP-T4 (9P), after 48 h of exposure, they did not decrease their anticorrosive performance until the end of the test. However, EP-Cr primers, despite showing delayed signs of oxidation (week 9; 9G), presented the worst performance towards the end of the test, reaching a degree of oxidation of 7G. The tendency of forming blisters of epoxy primers was low in the SO_2 chamber test. The only primer that developed blisters after 2184 h of testing was EP-Cr (6M). In the case of paint systems, blisters were formed at early hours of testing. Paint systems with zinc chromate-based primers developed large high frequency blisters (6MD after 1008 h) that caused partial severe blistering after 1344 h of testing.

The degree of blistering of the EP-T4-S (8MD) was similar to the case of EP-Cr-S systems (6MD). However, they did not cause delamination of the coating possibly because of the iron tannate complexes formation. EP-Ph-S (8F after 2500 h) and EP-T3-S (no blisters) systems presented the greatest resistance to blistering in the sulfur dioxide test. The degree of adhesion was similar for both primers and paint systems (Cr - T3 - T4, No.9 > Ph, No.8).

Conclusions

Epoxy primers pigmented with zinc tannates-based on Tara tannins were suitably formulated in the laboratory. Zinc chromate and modified zinc phosphate were used as conventional anticorrosive pigments for comparison purposes. Primers were applied on mild steel panels to compare their anticorrosive behavior in accelerated corrosion tests: Salt frog tests (3500 h) and Sulphur dioxide test (2500 h). The performance of paint systems containing the formulated epoxy primers was also studied.

Salt spray tests showed that epoxy primers pigmented with zinc tannates had similar performance to phosphate-based primers. Epoxy primers prepared with zinc chromate exhibited the worst anticorrosive behavior. Apparently, the development of blisters in primers with zinc tannates was reduced or avoided by the formation of iron tannate complexes. Epoxy primers in a paint system showed a better general performance. The same trend of anticorrosive behavior of epoxy primers was observed in the sulfur dioxide chamber: EP-Ph – EP-T3 > EP-T4 » EP-Cr. However, there was little presence of blisters in epoxy primers. Instead, a severe degree of blistering was developed by EP-Cr-S paint system, problem possibly interrupted by the formation of insoluble by-products in EP-T4-S samples. All epoxy primers, alone and as part of paint systems, in both accelerated corrosion tests, registered an outstanding degree of adhesion near the incision.

In conclusion, primers prepared with zinc tannates proved to have an equivalent (zinc phosphate) or superior (zinc chromate) anticorrosive performance on mild steel structures to primers containing conventional anticorrosive pigments. Zinc tannates can be considered potential green alternatives to traditional anticorrosive pigments for epoxy primers for the protection of structural steel.

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