Black wattle tannin as a zinc phosphating coating sealer

Rafael Silveira Peres, Eduardo Cassel, Carlos Arthur Ferreira and Denise Schermann Azambuja

This paper reports an investigation into the use of condensed black wattle tannin as an environmental friendly sealer after zinc phosphating of carbon steel. In order to verify the sealer efficiency against corrosion, electrochemical impedance spectroscopy, potentialdynamic polarisation and salt spray tests were performed. To verify the pore modifications and phase compositions, SEM, electron dispersive spectroscopy and X-ray diffraction analysis were carried out. The influence of the sealer on the adherence of finishing coatings was analysed. The results show that the tannin/sealer did not affect the final coating adhesion and improved the corrosion resistance of sealed samples. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: coating; phosphating; sealer; tannin; surface

Introduction

Phosphating is the treatment of ferrous and non-ferrous materials such as iron, steel, aluminium and magnesium to form an insoluble crystalline phosphate layer on the surface. This layer mainly improves corrosion resistance and paint adhesion on the substrate. All conventional phosphating processes are based on diluted phosphoric acid solutions with the presence of heavy or alkali metals ions. The most common types of phosphate coatings are based on zinc, iron and manganese.

Because of phosphate crystal growth, phosphate coatings have pores inherent to layer formation. This fact decreases the corrosion resistance of the substrate, because unprotected areas provide a path for corrosion attack. An alternative to increase corrosion resistance is sealing the pores once corrosion reactions are initiated at the coating/substrate interface.

Chromatising is the most effective conversion coating treatment used for sealing the pores of phosphating coatings. This treatment improves corrosion resistance due to the deposition of insoluble chromates in the pores and passivation of exposed metal. However, there are many environmental problems associated with Cr6+ and several alternatives have been proposed according to a review by Narayanan. However, many of the new sealing treatments use expensive and toxic reagents. Xu et al. used silicate solutions to post-seal hot-dip galvanised steel. Susac et al. applied the organosilane bis-1,2-(triethoxysilyl)ethane to sealing a 2024-T3 aluminium alloy, which had previously been coated by zinc phosphate. Banzeck et al. used a treatment with niobium ammonium oxalate to passivate of the pores of carbon steel (SAE 1010) after being phosphated in a zinc phosphating bath.

Tannins are natural and biodegradable polyphenolic compounds extracted from the bark, fruit and wood of several trees, including the black wattle tree (Acacia mearnsii De Wild.). The application of tannins in corrosion studies has been investigated and their efficiency is controversial. Tannins can convert active rust into compounds that are more stable and corrosion-resistant. Some authors have developed a tannin primer coating that exhibited excellent anticorrosive properties. On the other hand, the presence of hydrolysable tannins inhibits the formation of magnetite. Recent studies have shown that tannins can be good corrosion inhibitors for steel in acidic media due to the chemisorption mechanism. When Fe3+ ions react with tannins in aerated near neutral aqueous solution, a blue-black complex called ferric-tannate is formed. However, the ability of the ferric-tannates to protect against corrosion has not been resolved especially in long-term systems. These contradictory results may be related to the different types of tannins and different experimental conditions.

The aim of this study was to evaluate the use of tannin extracted from the bark of the black wattle tree as a natural, non-toxic and non-expensive long-term sealer of the zinc phosphating coating. Thus, this work intends to provide a specific and practice application of the black wattle tannin, evaluating the ferric-tannate behaviour beneath the organic coating. To the best of our knowledge, the application of the tannin as pore sealer has not been published yet, because the works cited before are based mainly in relative short-term inhibition studies and coatings formulation.

Experimental section

Material

All solutions and samples were prepared with analytical grade reagents. To prepare the zinc phosphating bath, zinc oxide...
(Vetec, Brazil), nitric acid (Merck, Germany), nickel sulphate (Vetec, Brazil) and phosphoric acid (Merck, Germany) were used. Sodium sulphate (VETEC, Brazil) was employed in the preparation of the electrolyte solutions to electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PP) experiments. A two-component epoxy primer (Intergard 269; Akzo Nobel, USA) was used as the finishing coating in adherence and salt spray tests. The black wattle tannin sample used in this work was supplied by TANAC (Montenegro, Brazil). The chemical composition of the carbon steel samples is given in Table 1.

Sample preparation

Samples of carbon steel were prepared by degreasing with an acetone/chloroform mixture (1:1), abraded with silicon carbide paper up to grade #1200, then degreasing and drying under a hot air stream. After the polishing and cleaning processes, the samples were immersed in zinc phosphating solution (Table 2) at 80 °C for 10 min. The samples were then rinsed thoroughly with deionised water and dried under a hot air stream.

Sealing process

After the zinc phosphating treatment, the samples were immersed in a solution of 6 g L⁻¹ of black wattle tannin for 40 min. At this concentration, the pH value of the solution was close to 6, which is optimal for the formation of ferric-tanninate. After 40 min, a blue-black residue was observed on the bulk of the bath and over the steel surface.

Surface analysis

The morphology of the phosphated steel surface was assessed by SEM (Philips model XL30) coupled to an Edax energy dispersive spectrometer (EDS). All samples were coated with a thin-gold layer prior to analysis. The phase identification of the phosphated sample was investigated by X-ray diffraction analysis (XRD) with a Philips diffractometer (model XPert MPD) using Cu Kα radiation. A step size of 0.02° was used to create X-ray patterns to identify the phases, which are in agreement with the literature. After the sealing treatment, the samples were investigated by X-ray diffraction with a Philips diffractometer (model XPert MPD) using Cu Kα radiation. A step size of 0.02° was used to create X-ray patterns to identify the phases, which are in agreement with the literature.

| Table 1. Chemical composition of carbon steel sample |
|-----------------|---|---|---|---|---|---|
| Element     | C | Mn | P | S | Cu | Cr |
| wt.%        | 0.103 | 0.46 | 0.013 | 0.096 | 0.01 | 0.18 |

Composition of zinc phosphating bath.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Concentration (g L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric Acid (H₃PO₄)</td>
<td>17.5</td>
</tr>
<tr>
<td>Nitric Acid (HNO₃)</td>
<td>20.0</td>
</tr>
<tr>
<td>Zinc Oxide (ZnO)</td>
<td>11.5</td>
</tr>
<tr>
<td>Nickel Sulphate (NiSO₄)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Electrochemical tests

Working electrodes were prepared from the phosphatised steel samples (25 × 15 × 1 mm). An area of 1.0 cm² was delimited by cold resin (epoxy) embedding.

A saturated calomel electrode (E = 0.241 V/NHE) was used as the reference electrode, and all potentials are referred to it. The auxiliary electrode was a Pt wire. The experiments were carried out under naturally aerated conditions at 25 °C. The electrochemical measurements were performed using an AUTOLAB PGSTAT 30 potentiostat (Echo Chemie, Netherlands) coupled to a frequency response analyser. The software used for the analysis of impedance spectra was NOVA 1.7 (Echo Chemie, Netherlands).

The PP curves were recorded at a scan rate of 1 mVs⁻¹. The corrosion potentials (Ecorr) and the polarisation resistances (RP) were calculated at a scan rate of 0.1 mVs⁻¹ with potential range of Ecorr ± 20 mV. This method was based on the ASTM G59[26] and ASTM G102[27] standards.

The EIS measurements were performed in potentiostatic mode at the open circuit potential. In this work, the open circuit potential after potential stabilisation is referred to as the corrosion potential, Ecorr. The amplitude of the EIS perturbation signal was 10 mV, and the frequency range studied was from 10⁵ to 10⁻¹ Hz.

Salt spray and painting adhesion test

The carbon steel samples (100 mm × 50 mm) were painted with an epoxy primer to a thickness of approximately 40 μm. Salt spray tests were performed according to the standard ASTM B117.[28] 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.

Adhesion measurements were made according to the ASTM D3359 standard test.[29] Eleven cuts (1 mm of distance) were made over the organic primer coating in two directions (perpendicular) in order to form squares. The number of the cuts and the distance between them were based on the standard. The sample surface was cleaned with a brush to eliminate residual coating generated in the cut process. After that, a Scotch-880 (3M, USA) tape was attached over the cuts with the assistance of an eraser. The tape was pulled off with an angle near 180º in relation to the sample. The number of the detached primer coating was compared with the standard, being classified in five degrees (5B to 0B). The highest degree (5B) corresponds to no removal of the primer, whereas the lowest degree corresponds to more than 70% of primer removal.

Results and discussion

Characterisation of phases in the phosphate layer and morphology

The phase compositions of the phosphate coating formed on carbon steel before and after the sealing treatment were analysed by XRD as shown in Fig. 1. The phosphate coating before the treatment with tannin (Fig. 1a) consisted mainly of Zn₃(PO₄)₂·4H₂O (hopoite) and Zn₃Fe(PO₄)₂·4H₂O (phosphophylite) phases, which are in agreement with the literature.[30] After the sealing process (Fig. 1b), the phosphate coating shows no substantial difference in the phase composition. Thus, the sealing bath (described before) does not affect the coating.
The amorphous nature of ferric-tannate could be confirmed once no additional peak was observed in the X-ray diffraction patterns (Fig. 1).

The surfaces of the samples were analysed by SEM in backscattering electrons mode. The SEM micrograph and corresponding EDS for several areas in the unsealed samples are given in Fig. 2 and the sealed samples are given in Fig. 3. The light areas show the steel surface without phosphate crystals and the dark areas correspond to the zinc phosphate crystals that formed during the phosphating process, as shown in the EDS spectra (Figs. 2 and 3). Only the EDS spectra of the light areas in the sealed sample showed the presence of carbon (Fig. 3). Furthermore, the presence of a cracked layer in the pores (light areas) can be attributed ferric-tannate layer formation (Fig. 3).

**Electrochemical tests**

The anticorrosion efficiency of the sealed samples was evaluated by PP and EIS. The PP curves of sealed and unsealed phosphatised steel samples were performed in aerated 0.1 mol L\(^{-1}\) Na\(_2\)SO\(_4\) solution after 4 h of immersion (Fig. 4).

According to (Fig. 4), the anodic and cathodic current densities decreased when the phosphate steel was sealed. The presence of black wattle tannin as a sealer shifted the \(E_{\text{corr}}\) to a more positive value.

The corrosion current densities \(j_{\text{corr}}\) in Table 3 were calculated from the extrapolation of the anodic and cathodic Tafel lines (Fig. 4).

According to Table 3, the polarisation resistance \(R_p\) showed the highest value \(18.85 \text{k} \Omega \text{cm}^{-2}\), and the \(j_{\text{corr}}\) value decreased significantly in the sealed sample. This fact could be attributed to the ferric-tannate layer formed over the pores, evidencing the protective character of this treatment.

To complement the PP data, EIS measurements were performed with the phosphatised steel samples in aerated 0.1 mol L\(^{-1}\) Na\(_2\)SO\(_4\) after 4 h of immersion. The experimental and fitted EIS data are shown in (Figs. 5 and 6). According to Fig. 6, the Bode plots show two time constants whose maximum phase angle was around \(-50^\circ\), attributed to the process under mass transport control, characteristic of phosphating layers.

The equivalent circuit (Fig. 7) proposed by fitting the EIS diagrams is \(R_s\left(CPE_1R_1\right)\left(CPE_2R_2\right)\), where \(R_s\) represents the ohmic resistance between the reference and the working electrode and \(R_1\) and \(R_2\) represent the charge transfer resistance in physical meaning. The capacitance was replaced by a constant phase element \((CPE)\) that describes a non-ideal capacitor when the phase angle is different from \(-90^\circ\). The \(CPE\) impedance is attributed to the distributed surface reactivity, surface heterogeneity and roughness of the current and potential distribution, which in turn are related to the electrode geometry and the electrode porosity. The \(CPE\) impedance is given by equation 1.\(^{[34]}\)
\[ Z_{\text{CPE}} = Q(j\omega)^n \]  

where \( Z_{\text{CPE}} \) is the impedance and \( \omega \) is the angular frequency. The parameters \( n \) and \( Q \) are independent of frequency. The CPE represents a capacitor for \( n = 1 \), a resistor for \( n = 0 \) and a diffusion process for \( n = 0.5 \).

In Fig. 7, two time constants are presented: \( R_1\text{CPE}_1 \) related to the inner conversion layer and \( R_2\text{CPE}_2 \) to the outer porous...
For these layers, the capacitance was replaced by a CPE due to the coating characteristics. In this case, the overall impedance is given by the sum of the two layers corresponding to the impedance values and is characterised by a parallel combination of the capacitance and resistance of each layer, as proposed in the literature.

The fitting quality was evaluated based on error percentage associated with each component, showing errors smaller than 5%. The software used to simulate the EIS data was NOVA 1.7 (Echo Chemie, Netherlands). The simulated data obtained from the fittings are given in Table 4.

According to Table 4, the sealing treatment with tannin promotes the increase of the resistance and the decrease of the capacitance improving the corrosion resistance of this treatment. These results are in agreement with the PP results (Table 3) showing the protective character of the formed layer.

Adhesion tests

Adhesion tests were performed to evaluate the influence of the sealer on the adherence of organic coatings on the phosphatised steel. The adhesion of the primer coating on the unsealed and sealed phosphatised samples was measured using a tape test\(^{29}\). The results are summarised in Table 5.

According to Table 5, the adhesion rating for sealed and non-sealed phosphating coatings was 4B, equivalent to less than 5% primer coating removal. For the unphosphatised sample, the adhesion rating was 1B, equivalent to 35%–65% primer coating removal. The results show that the addition of the sealer did not affect the adherence of paint to the phosphatised substrate.

Salt spray tests

To verify the influence of the sealer on the corrosion resistance of the coating/phosphating system, salt spray tests were performed.\(^{28}\) Epoxy coatings on unphosphatised, phosphatised and tannin/sealed phosphatised carbon steel samples were tested. Prior to salt spray tests, the organic coating was scratched to expose the substrate. The duration of the salt spray tests was 672 h. Figure 8 shows samples exposed to 672 h of salt spray. Evident signs of intense corrosive attack (Fig. 8a) were associated with the unphosphated sample. The unsealed phosphatised sample (Fig. 8b) presented bubbles (corrosive attack) over the entire sample.

**Figure 6.** Bode plots of unsealed (□) and sealed (●) phosphate steel samples immersed in aerated 0.1 mol L\(^{-1}\) Na\(_2\)SO\(_4\) solution for 4 h. The solid black line (—) represents the fitting data.

**Figure 7.** Equivalent electric circuit proposed to simulate the experimental data of phosphated steel samples immersed in 0.1 mol L\(^{-1}\) for 4 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Equivalent circuit</th>
<th>Fitting parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Sealed</td>
<td>(R_s (\Omega \text{ cm}^2)) (R_1 (\Omega \text{ cm}^2))</td>
<td>(R_2 (\Omega \text{ cm}^2))</td>
</tr>
<tr>
<td>Sealed</td>
<td>(R_s (\Omega \text{ cm}^2)) (R_1 (\Omega \text{ cm}^2)) (R_2 (\Omega \text{ cm}^2))</td>
<td>(R_3 (\Omega \text{ cm}^2))</td>
</tr>
</tbody>
</table>

**Table 4.** Fitting parameters used to simulate the electrochemical impedance spectroscopy plots for unsealed and sealed phosphate steel samples immersed in aerated 0.1 mol L\(^{-1}\) Na\(_2\)SO\(_4\) solution for 4 h

<table>
<thead>
<tr>
<th>Sample</th>
<th>Equivalent circuit</th>
<th>(R_s (\Omega \text{ cm}^2))</th>
<th>(R_1 (\Omega \text{ cm}^2))</th>
<th>(R_2 (\Omega \text{ cm}^2))</th>
<th>(n_1)</th>
<th>(n_2)</th>
<th>(R_3 (\Omega \text{ cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Sealed</td>
<td>(R_s (\Omega \text{ cm}^2)) (R_1 (\Omega \text{ cm}^2)) (R_2 (\Omega \text{ cm}^2))</td>
<td>15.36</td>
<td>2.71 \times 10^{-3}</td>
<td>0.62</td>
<td>0.196</td>
<td>4.36 \times 10^{-4}</td>
<td>0.65</td>
</tr>
<tr>
<td>Sealed</td>
<td>(R_s (\Omega \text{ cm}^2)) (R_1 (\Omega \text{ cm}^2)) (R_2 (\Omega \text{ cm}^2)) (R_3 (\Omega \text{ cm}^2))</td>
<td>17.21</td>
<td>7.43 \times 10^{-4}</td>
<td>0.39</td>
<td>1.230</td>
<td>1.30 \times 10^{-4}</td>
<td>0.69</td>
</tr>
</tbody>
</table>

**Table 5.** Comparison of the adhesion ratings of the primer coating in the phosphatised samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Primer thickness ((\mu\text{m}))</th>
<th>Mean (\pm) SD* ((n = 6))</th>
<th>Adhesion rating (ASTM D3359)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unphosphatized</td>
<td>41 (\pm) 0.5</td>
<td>1B</td>
<td></td>
</tr>
<tr>
<td>Phosphatized</td>
<td>40 (\pm) 0.5</td>
<td>4B</td>
<td></td>
</tr>
<tr>
<td>Sealed and phosphatized</td>
<td>42 (\pm) 0.4</td>
<td>4B</td>
<td></td>
</tr>
</tbody>
</table>

* Standard deviation
surface. On the other hand, the tannin/sealed phosphatised samples presented bubbles only in the areas where the substrate was exposed (scratched area), showing an improvement in corrosion protection. In this case, the ferric-tannate used as sealer showed long-term protection against corrosion. The use of ferric-tannate layer concomitantly with organic coatings improves the overall resistance against the corrosion.

Conclusions

The effect of black wattle tannin as a natural and non-toxic sealer after phosphating treatment of carbon steel was evaluated in this study. XRD confirmed that the ferric-tannate is amorphous and the phosphate coating formed on carbon steel consisted mainly of hopeite and phosphophylite. The SEM and EDS analyses showed ferric-tannate layer formation on the exposed steel surface (pore). Electrochemical and salt spray experiments showed an improvement in the corrosion resistance of the sealed phosphate coating. The adhesion tests indicate that the addition of the sealer did not affect the adherence of paint to the phosphatised substrate. Thus, black wattle tannin can be used as an environmental friendly sealer in the zinc phosphating bath through a simple and cheap process.

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