

# Lanthanum Derivative from “Tara” Tannin for Steel Temporary Protection

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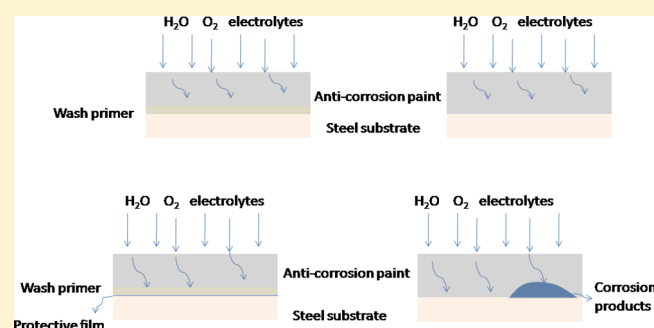
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## Supporting Information

**ABSTRACT:** Tannins are extracted from certain plants and contain numerous phenol groups. They may be employed, together with their derivatives, to formulate protective coatings due to their inhibitive properties. The objective of this research was to synthesize lanthanum “tannates”, to formulate wash-primers. Two “Tara” (*Caesalpinia spinosa*) tannins and 0.1 M  $\text{La}(\text{NO}_3)_3$  were employed to obtain the corresponding tannates. The inhibitive action of the tannates was evaluated by linear polarization and corrosion potential measurements employing a SAE 1010 electrode. Lanthanum tannates were used to formulate wash-primers whose anticorrosion performance was evaluated by corrosion potential and ionic resistance measurements. The primers were incorporated in alkyd paint systems and their anticorrosion performance was tested in the salt spray chamber and by electrochemical impedance spectroscopy. Lanthanum tannate primers protected steel and behaved in a similar way to that formulated with zinc tetroxychromate.



## 1. INTRODUCTION

Metallic structures and machinery normally possess bare surfaces which need temporary anticorrosion protection prior to their use. In many cases, this temporary protection is required during the fabrication process. Finished metallic parts also need some kind of protection during shipping or storage in different atmospheres.

Many different temporary protective systems are described in the literature.<sup>1</sup> A wash-primer is a multifunctional protective system which deposits a conversion coating onto the metal surface.<sup>2,3</sup> It can be applied on steel, stainless steel, aluminum, galvanized steel, etc. to give a dry film whose thickness is comprised between 8 and 13  $\mu\text{m}$ . The function of wash-primer is to passivate metallic surfaces to temporarily protect the metal and, finally, allow the application and adhesion of a full bodied primer; particularly in the case of those difficult-to-paint metals like aluminum or galvanized steel. Wash-primers are formulated with an inhibitive pigment, currently zinc tetroxychromate, and phosphoric acid to phosphatise the metal surface. However, chromates are questioned because their negative impact on the environment and on humans' health.<sup>4</sup> The binder is polyvinylbutyral resin in a water and alcohol mixture.

Tannic acid and tannins may be considered as eco-friendly inhibitors which could replace chromates. Tannins are extracted from different parts (bark, root, leaves, and fruits) of certain plants and contain numerous phenol groups. The disposition of

these phenolic groups in the molecule enables the complexation of metallic ions, especially iron ions to form iron “tannate” films thus converting the metal surface generating a protective film.<sup>5,6</sup> This reaction is better accomplished in the presence of phosphoric acid.<sup>7–12</sup> Tannins extracted from a great variety of trees were used to protect metals. The most employed ones were obtained from the following plants: mimosa,<sup>6,9,10</sup> chestnut,<sup>7,12</sup> pine,<sup>13</sup> “quebracho”,<sup>14</sup> mangrove,<sup>15,16</sup> etc. New tannins are being proposed as a consequence of the reconnaissance and further exploitation of woods and forests continues.<sup>17</sup>

Tannic acid was found to inhibit steel corrosion in acid media by the formation of an iron tannate film. Its inhibitory efficiency is higher than 89%.<sup>14,18</sup>

It was demonstrated that “Quebracho” (*Schinopsis* sp.) and “Mimosa” tannins are mixed inhibitors because they influence both reactions, the anodic and the cathodic ones. The inhibitive action of these tannins decreased as the pH increased.<sup>14,18</sup>

The protection of the metal surface by tannins is affected negatively by chlorides which turned the metal surface more

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active. No passivity could be achieved when the chloride concentration is increased beyond  $500 \text{ mg}\cdot\text{m}^{-2}$ .<sup>19</sup>

There is a great variety of commercial products which are claimed to stabilize and/or transform the surface oxide layer. As a trend, these products contain tannins but it was suggested that they did not possess the same anticorrosion behavior of a classical primer containing chromates.<sup>20</sup> These products are designed to be applied on poorly prepared surface to transform the adherent oxide layer. The conversion layer was mainly composed of a magnetite whose stoichiometry differs from that normally found.

The employment of tannins in formulations to be applied on corroded metals did not lead to conclusive results; however, the authors found that they may improve the anticorrosion performance of the painting system as a whole.<sup>7,12,20,21</sup>

Tannin derivatives, often called tannates, with proved anticorrosion efficiency, have been developed and employed in anticorrosion paints. The word "tannate" refers to any salt or ester of tannic acid. Giúdice et al. carried out pioneer investigations on the employment of metallic tannates in anticorrosion paints with promising results.<sup>22–24</sup> More recently, the employment of zinc tannates with improved protective performance was reported.<sup>25,26</sup> These tannates were obtained employing "Tara" tannin. Zinc tannate obtained from Tara tannin seemed to be an effective antifouling pigment for marine coatings.<sup>27</sup> Tara (*Caesalpinia spinosa*) is a small leguminous tree which is abundant in Peruvian territories and may be found distributed worldwide. Gallotannins are the main constituent of Tara tannins (53%) and may be obtained from the plant extract by alkaline hydrolysis.<sup>28,29</sup>

The purpose of this investigation was to formulate an eco-friendly wash-primer containing lanthanum tannate (LT) instead of zinc tetroxychromate. This last pigment is toxic and carcinogenic, whereas the toxicity of LT is low. Lanthanum tannate may be considered as belonging to the so-called fourth generation of corrosion inhibitive pigments. This generation of pigments is constituted by hybrid organic/inorganic pigments which are the result of the combination of an organic compound with inorganic species.<sup>30</sup> There is a great variety of organic compounds which may be employed to develop these type of inhibitors: surfactants,<sup>31</sup> organic compounds like those with O, N, S, P, and/or  $\pi$  electrons;<sup>31</sup> carbohydrate polymers,<sup>32</sup> plant extracts,<sup>30,32</sup> etc. The most commonly employed inorganic species are zinc cation,<sup>30,33</sup> lanthanide cations,<sup>34,35</sup> sodium nitrite,<sup>36</sup> potassium halides,<sup>37</sup> etc.

LT was synthesized in the laboratory by treating a suspension of Tara tannin with lanthanum salts. Lanthanum compounds inhibit the cathodic reaction on different metals by the precipitation of the sparingly soluble hydroxide.<sup>38,39</sup> The protective behavior of LT and that of the wash-primer containing this pigment were both evaluated by electrochemical techniques. In a second stage, the wash-primer was integrated in a complete coating scheme whose anticorrosion performance was assessed by electrochemical impedance spectroscopy (EIS) and accelerated tests (salt spray and humidity chambers). It was shown that the protective efficiency of LT was  $\sim 94\%$ ; so it can be employed as an effective inhibitor in a wash-primer in order to replace chromates. The as formulated wash-primer performed satisfactorily in electrochemical and accelerated tests.

## 2. MATERIALS AND METHODS

**2.1. Synthesis and Characterization of LT.** Two commercial Tara tannins were selected for this research. One of them, T40, is a tannin obtained by extraction with ethanol, whereas the other, T80, was extracted with more polar solvents like acetone. From now on, Tara tannins will be referred to as "TT" and their derivatives precipitated with lanthanum salts as "LT". The number "40" and "80" will indicate the extraction performed with different solvents.

Solutions of TT40 and TT80 were prepared from 10 g of the corresponding commercial Tara tannins by extraction with 300 mL of distilled water (DW) at  $90^\circ\text{C}$  during 1 h. Stirring was continued for 24 h; then, the solids were filtered off and the solutions were brought to a final volume of 1000 mL with DW. Then, 50 mL of the as prepared solutions were mixed with increasing volumes of  $\text{La}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$  0.1 M at pH 8, under continuous stirring for 1 h. The precipitate obtained in each case was washed with DW and allowed to dry during 24 h at  $100^\circ\text{C}$ . The LT precipitation curves were obtained in this way to select the respective synthetic pathways of LT40 and LT80 pigments. The as obtained precipitates were characterized by FTIR spectroscopy by means of a PerkinElmer Spectrum One Spectrometer. FTIR spectra were used to control that undesirable substances (like oxides) did not precipitate together with LT after the addition of the lanthanum salt.

In order to obtain the mass of La(III) that reacted with Tara tannin, the LT precipitate was heated at  $850^\circ\text{C}$ . The solid obtained after calcination was identified by XRD as  $\text{La}(\text{OH})_3$  (JCPDF# 36–1481). The content of tannin in the saturated solution was determined employing Folin-Denis reagent.<sup>27,40,41</sup> The concentration of La(III) in this solution was determined by the oxalate method followed by further calcination of the precipitate at  $900^\circ\text{C}$  which was weighed as the corresponding oxide.<sup>42</sup>

The inhibitive properties of LT40 and LT80 were assessed by electrochemical techniques in the corresponding pigment suspensions in NaCl 0.1M. The pigments suspensions were prepared by dispersing 1.0 g of each pigment in 100 mL of the supporting electrolyte with continuous stirring during 1 day to achieve complete saturation. The corrosion potential of a SAE 1010 steel electrode was measured as time elapsed, with respect to a reference, the saturated calomel electrode (SCE). The polarization resistance technique<sup>43,44</sup> was employed to obtain corrosion rates with a three electrode cell. A SAE 1010 steel rod (area:  $0.28 \text{ cm}^2$ ) was the working electrode, the SCE the reference and a Pt mesh the counterelectrode. The sweep amplitude was  $\pm 20 \text{ mV o.c.}$  and the scan rate  $0.5 \text{ mVs}^{-1}$ . All electrochemical measurements were done with a GAMRY Interface 1000 potentiostat in normally aerated solutions stirred at 300 rpm. A cell like that described previously was used to obtain polarization curves but in a wider potential range;  $\pm 250 \text{ mV oc.}$

In every case, the behavior of the steel electrode in Tara tannin suspensions were also carried out for concentrations of tannin comprised between 2 and 12 ppm.

**2.2. Elaboration and Application of Wash-Primers Containing LT and an Alkyd Paint System.** The wash-primer was prepared on the basis of a tetroxychromate formulation reported elsewhere<sup>45</sup> which consisted of two components called part A and part B. The model primer contained zinc tetroxychromate as the inhibitive pigment and phosphoric acid. The dispersion of the film forming material,

Table 1. Wash Primers Composition

	formulation v/v %	TT 40	LT 40	TT 80	LT 80	Talc	ZTC
part A	polyvinyl butyral resin	8.20	8.20	8.20	8.20	8.20	8.20
	pigment	2.20	2.20	2.20	2.20		2.20
	talc	0.47	0.47	0.47	0.47	2.67	0.47
	carbon black	0.05	0.05	0.05	0.05	0.05	0.05
	butanol	22.79	22.79	22.79	22.79	22.79	22.79
	isopropanol	64.16	64.16	64.16	64.16	64.16	64.16
	water	2.13	2.13	2.13	2.13	2.13	2.13
part B	citric acid	17.1	17.1	17.1	17.1	17.1	17.1
	water	14.0	14.0	14.0	14.0	14.0	14.0
	isopropanol	68.9	68.9	68.9	68.9	68.9	68.9
	PVC	0.25	0.25	0.25	0.25	0.25	0.25

the polyvinyl butyral resin,<sup>46</sup> and the anticorrosion pigments constituted part A of the primer while phosphoric acid and solvents are stored as part B. Zinc tetroxychromate was replaced, by volume, by the anticorrosion pigments LT40 and LT80 respectively to formulate the more eco-friendly wash-primer. Phosphoric acid needed to be replaced by citric acid to avoid the precipitation of lanthanum phosphate. The composition of both parts of the primer, part A and part B, is sketched in Table 1. As the properties of the coatings depend on the pigment volume concentration and its relationship with the critical pigment volume concentration (CPVC),<sup>47–49</sup> the composition of the primer was given by volume. The components of the Part A were dispersed in a ball mill during 24 h to achieve an acceptable dispersion degree (5 in Hegman gage). Solvents and citric acid were mixed to obtain Part B. Other primers formulations were obtained employing Tara tannin (TT40 and TT80) or talc which was used as control together with the chromate wash-primer. Sandblasted SAE 1010 steel panels were degreased with toluene before painting and part A and B were mixed as 4:1 by weight, respectively. The primers were applied by brushing. The final dry film thickness was  $7 \pm 2 \mu\text{m}$ .

The anticorrosion behavior of the formulated wash-primers was studied by electrochemical techniques: corrosion potential and ionic resistance variations were measured as a function of time. The ionic resistance was obtained with a Pt counter-electrode employing an ATI ORION model 170 conductimeter, at 1000 Hz. The corrosion rate of primed steel was also determined following the procedure described in the preceding paragraph. Taking into account that the primers possessed low ionic resistance, it was possible to determine the corrosion rates by the linear polarization method.<sup>50</sup>

Primed steel panels were submerged 24 h in DW. Afterward, the coating was removed with a suitable solvent, like acetone, to observe the morphology of the protective layer formed on steel panels by means of a scanning electron microscope (SEM), FEI Quanta 200 with tungsten filament. The surface elemental composition of the protective film formed on steel panels was determined with an energy dispersive RX microanalyzer and the EDX detector Apollo 40.

**2.3. The Performance of the Wash-Primer in an Alkyd Paint System.** **2.3.1. Formulation, Elaboration, and Application of the Alkyd Paints.** The anticorrosion behavior of the wash-primers was assessed by incorporating them in a complete painting scheme constituted by the primers, an anticorrosion alkyd paint and a top coat alkyd coating. The dry film thickness of each alkyd coat was  $35 \mu\text{m}$ .

The binder employed to formulate the coatings was a solvent-borne-medium oil alkyd (50% linseed oil, 30% o-phthalic anhydride, 8% pentaerythritol and glycerol and 12% pentaerythritol resinate). The solvent was white spirit. It was decided to check the anticorrosive properties of the pigments employing solvent borne paints because their behavior has been well documented for many years. The PVC/CPVC relationship was 0.8 as suggested in previous researches.<sup>51,52</sup>

The composition of the anticorrosive paint, expressed as percentage by volume, was: zinc molybdenum phosphate, 6.54%; non fibrous magnesium silicate, 6.37%; barite, 6.20%; titanium dioxide, 2.55%; alkyd resin: white spirit (1:1), 60.23% and solvents, 18.11%. The topcoat composition v/v % was: titanium dioxide, 10.8%; alkyd resin: white spirit (1:1), 66.2%; and solvent, 23%. All pigments were dispersed 24 h in the vehicle, employing a ball mill to achieve an acceptable dispersion degree.

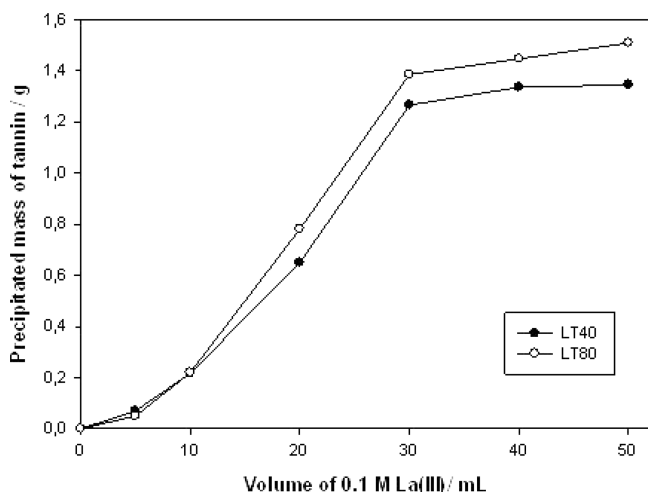
**2.3.2. The Performance of Anticorrosive Paints through Accelerated Tests.** A set of three panels was placed in the salt spray chamber (ASTM B 117) to evaluate the rusting and the blistering degrees (ASTM D 610 and ASTM D 714, respectively). Painted panels were evaluated during 90 days. The mean value of the obtained results was reported in this paper. Similar panels were placed in the humidity chamber (ASTM D 2247); and blistering and rusting degrees were evaluated during 30 days.

Impedance spectra of painted panels were performed in the potentiostatic mode, at the corrosion potential ( $E_{\text{corr}}$ ). Two acrylic tubes were attached to each coated panel (working electrode) with an epoxy adhesive; the area exposed to the electrolyte, in each cell, was  $15.9 \text{ cm}^2$ . Measurements were carried out as a function of the exposure time in 3% NaCl, using the 1255 Solartron FRA and the 1286 Solartron EI. A large area Pt–Rh mesh of negligible impedance and saturated calomel (SCE) were employed as auxiliary and reference electrodes, respectively. The amplitude of the applied AC voltage was 0.010 V peak to peak. The frequency range employed was  $1 \times 10^5 \text{ Hz} \leq f \leq 1 \text{ Hz}$ . The experiments were carried out at laboratory temperature ( $20 \pm 2 \text{ }^\circ\text{C}$ ), using a Faraday cage. The experimental impedance spectra were interpreted on the basis of equivalent electrical circuits using the procedure developed by Boukamp.<sup>53</sup> Simultaneously, corrosion potential values were recorded as a function of immersion time.

### 3. RESULTS AND DISCUSSION

#### 3.1. Pigment Preparation and Characterization.

Previous research shows the convenience of precipitating LT at pH 8.<sup>54</sup> The two precipitation curves (LT40 and LT80) were similar. The mass of precipitated lanthanum tannate increased as the added volume of 0.1 M  $\text{La}(\text{NO}_3)_3$  increased but both curves reached a “plateau” when 30.0 mL of  $\text{La}(\text{III})$  solution were added. This volume is the adequate one to precipitate the corresponding lanthanum tannates from 50 mL of tannin solution. Beyond this volume, the amount of precipitated tannate did not increase significantly. The mass of precipitate was a little higher for TT80 (Figure 1). According to previous



**Figure 1.** Mass of tannin precipitated as a function of the volume of 0.1 M  $\text{La}(\text{NO}_3)_3$  at pH 8.

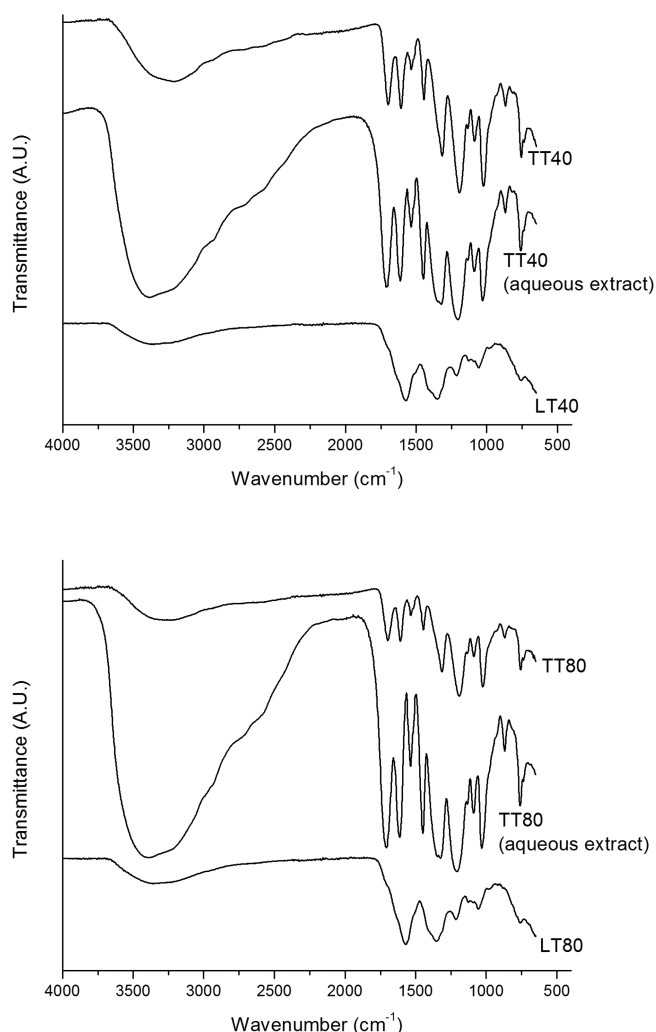
results, the precipitation of the corresponding tannates was accomplished by mixing 50 mL of the tannin solution with 30.0 mL of 0.1 M  $\text{La}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$  0.1 M at pH 8, under continuous stirring during 1 h. The precipitate obtained in each case was washed with DW and dried for 24 h at 100 °C.

The main components of Tara tannins are gallotannins (~53.1%). They may also contain ellagitannins (~6.9%) and gallic acid (~9.5%);<sup>28</sup> in this sense it was expected that FTIR spectra of TT40 and TT80 Tara tannins were similar to each other (Figure 2). Both spectra presented the same set of absorption bands. Band assignment was accomplished by a suitable chart published elsewhere.<sup>55–57</sup>

A wide band associated with the OH stretching from different chemical environments was observed for the region 3600 to 3000  $\text{cm}^{-1}$  which is characteristic of the polyphenolic extracts. As a consequence of the great number of phenolic groups the absorption band is wide and the three bands in the range 3100–3000  $\text{cm}^{-1}$ , characteristics of the aromatic ring, could not be appreciated in the corresponding spectra. The band in this region was broader in the case of the aqueous extract due to the hydration of both tannins.

The band located at 1690  $\text{cm}^{-1}$  could be attributed to ester unions which are the result of the esterification of gallic acid units and a hydroxyl group from a polyol as it occurs in gallotannins and ellagitannins.

Bands related to the vibrations of the  $\text{C}=\text{C}$  aromatic bond at 1610, 1537, and 1455  $\text{cm}^{-1}$  were also detected for both tannins. Actually, four bands could be detected in the 1450–1600  $\text{cm}^{-1}$



**Figure 2.** FTIR spectra of tannins (TT40 and TT80), their aqueous extracts and their derivatives (LT40 and LT80).

but, sometimes, the band at 1580  $\text{cm}^{-1}$  overlapped with the band at 1610  $\text{cm}^{-1}$ .

The stretching of C–O groups present in ester linkages were detected at 1318, 1203, and 1024  $\text{cm}^{-1}$ . The deformation of the aromatic C–H bond in the plane was located at 1138 and 1097  $\text{cm}^{-1}$ , respectively, whereas the band corresponding to the C–H deformation out of the plane was found at ~830  $\text{cm}^{-1}$ .

Spectra of the dried extracts were similar to those of the tested tannins, TT40 and TT80, respectively.

As it occurred with tannins, the FTIR spectra corresponding to the tannates are similar to each other and they maintain a certain relationship with those of TT40 and TT80 Tara tannins. However, some changes were observed. As the ester bonds hydrolyzed at pH 8 at which lanthanum tannates were prepared, the band at 1690  $\text{cm}^{-1}$  disappeared. In change, two broad absorption bands centered at 1573 and 1339  $\text{cm}^{-1}$  appeared. The first band was attributed to the carboxylate anion formed after hydrolysis. This group reacted with  $\text{La}(\text{III})$  to form the corresponding tannate. The other absorption band was assigned to the C–OH vibration. Some of the absorption bands present in the tannin spectra, close to these new bands, appeared as shoulders of them (Figure 2). The  $\text{La}_2\text{O}_3$  absorption bands, which are normally found at 464 and 571



$\text{cm}^{-1}$ , are not observed. This fact confirmed that lanthanum tannate is precipitating instead of lanthanum oxide.

The solubility of tannin as determined by the Folin-Denis reagent was lower than 1 ppm for both tannates. The concentration of  $\text{La(III)}$  in the saturated solutions was very low ( $<2.2 \times 10^{-6} \text{ M}$ ) because it was completely precipitated to form LT40 and LT80. As no precipitate was formed by the oxalate method to determine La, it was concluded that the  $\text{La(III)}$  content was under the detection limit. The content of  $\text{La(III)}$  in LT40 and LT80 was determined by calcination and it was found to be 26.0% for LT40 and 28.0% for LT80. This fact indicated that both LT40 and LT80 can act as a reservoir of  $\text{La(III)}$ .

As a trend, for both tannins, at a given immersion time,  $E_{\text{corr}}$  increased as the concentration of tannin increased. None of the solutions seemed to inhibit satisfactorily steel corrosion, the lowest corrosion rates were obtained with the most diluted solution (2 ppm). In many cases, tannin solutions were more aggressive than the supporting electrolyte. This behavior could be explained taking into account the pH 3 of the TT suspensions and is in complete agreement with results of  $E_{\text{corr}}$  measurements. In change, steel  $E_{\text{corr}}$  was highly reduced in the tannate suspensions. LT obtained from Tara tannin TT40 was more effective than the other tannate. The inhibitive efficiency, in the case of lanthanum tannate obtained with Tara tannin TT40, was 95% after 24 h while this efficiency matched 86% for the LT precipitated from Tara tannin TT80 (Supporting Information (SI) Table S1).

Steel  $E_{\text{corr}}$  in TT solutions was displaced, with respect to the blank (steel in the supporting electrolyte), to more negative values. The displacement may be higher than 200 mV, particularly at the beginning of the test period. This fact may be attributed to the low pH of the TT solutions (pH 3). In every case steel was active, dissolving itself to generate a film of iron tannate. In this sense, it is interesting to point out that, during the first minutes of immersion,  $E_{\text{corr}}$  of steel was very negative and increased as time elapsed. However, there are no significant differences among the three concentrations of TT40 employed in this assay and, at the end of the test,  $E_{\text{corr}}$  fluctuated around  $-0.600 \text{ V}$ . In change, steel  $E_{\text{corr}}$  values in the lanthanum tannate suspension revealed that the substrate became passivated. At the beginning of the exposure time and during 50 min  $E_{\text{corr}}$  increased from around  $-0.300 \text{ V}$  to finally fluctuate around  $-0.216 \text{ V}$  (Figure 3). TT80 presented a similar behavior but steel  $E_{\text{corr}}$  in LT80 suspensions resulted  $\sim 0.100 \text{ V}$  more negative than in the case of LT40 (Figure 4).

Polarization curves showed that, in the presence of tannates, steel is active. In change, lanthanum tannates restrained steel dissolution. The cathodic current is also lower in the presence of these tannates (SI Figure S1).

**3.2. Wash-Primer Characterization.** The primer containing zinc tetroxychromate (ZTC) displaced steel  $E_{\text{corr}}$  to more positive values with respect to the other primers. All the primers formulated with a TT or its derivative showed a similar behavior. At the beginning of the test period, very negative potentials were measured and they may be related to metal dissolution and the formation of a protective film mainly composed by iron tannates. This displacement was more important in the case of the primer containing LT. As time went on,  $E_{\text{corr}}$  decreased for the ZTC primer, and it increased for the other primers, so at the end of the testing period the values did not differ significantly. In every case,  $E_{\text{corr}}$

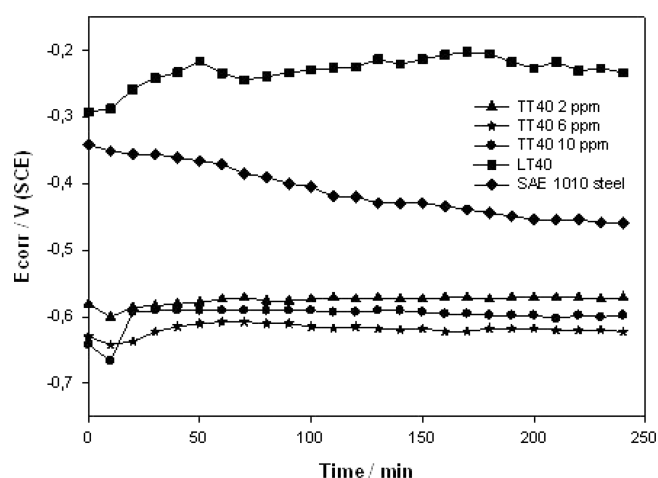


Figure 3. Steel corrosion potential in TT40 and LT40 suspensions in 0.025 M NaCl.

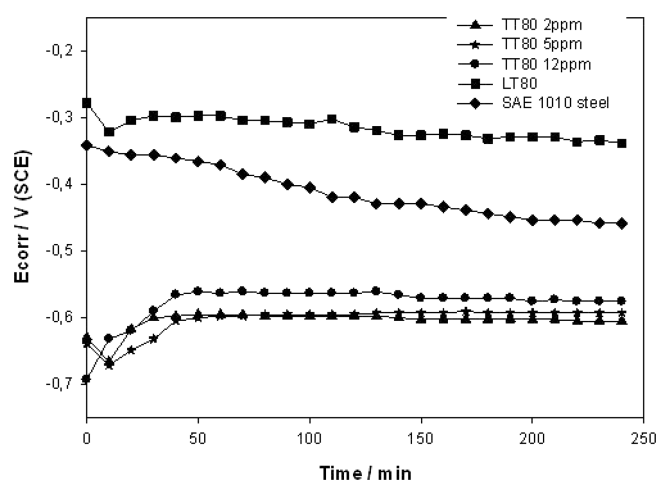


Figure 4. Steel corrosion potential in TT80 and LT80 suspensions in 0.025 M NaCl.

corresponded to the formation of iron oxides which grew together with iron tannates (Figures 5 and 6).

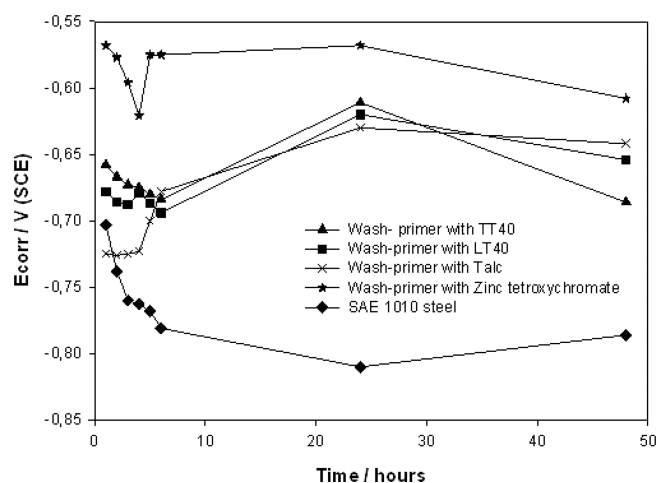
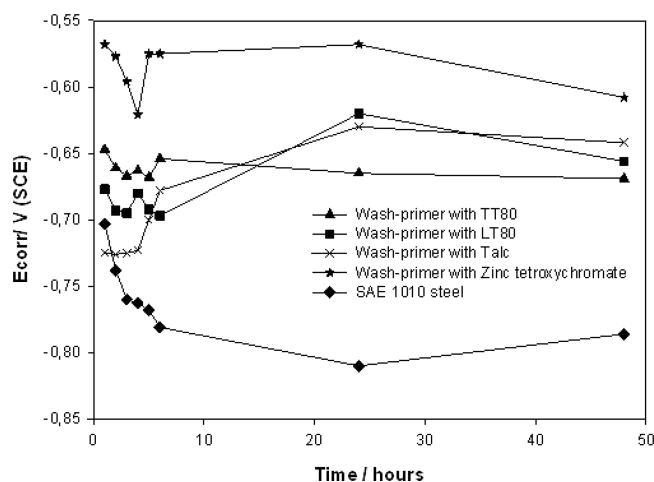
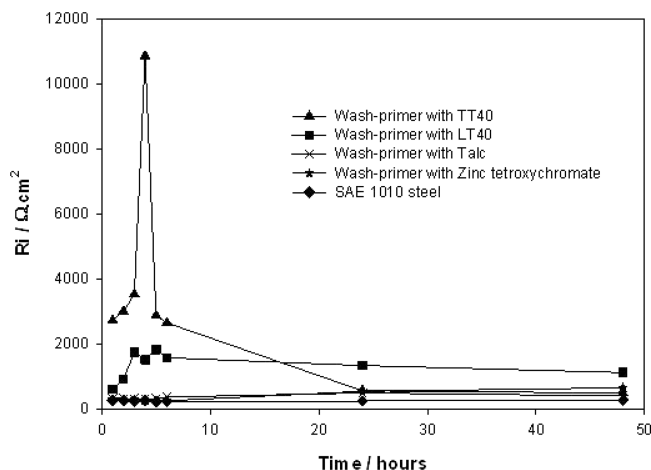


Figure 5. Steel corrosion potential of primed panels with TT40 or its derivative LT40, as a function of time in 0.025 M NaCl.



**Figure 6.** Steel corrosion potential of primed panels with TT80 or its derivative LT80, as a function of time, in 0.025 M NaCl.

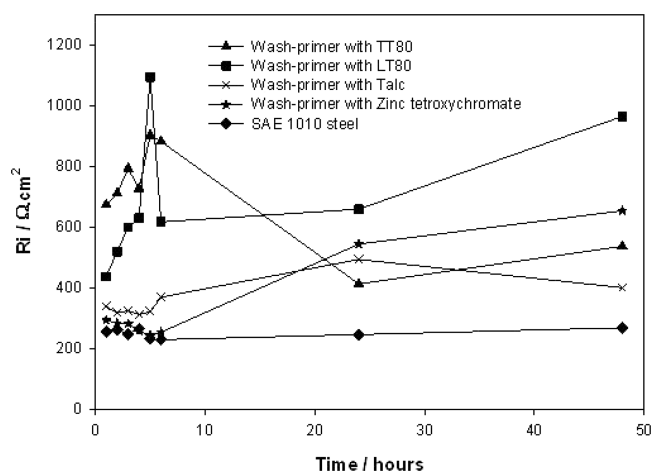
None of the tested system possessed barrier properties; so, the control of the corrosion process was mostly, in nature, kinetic.<sup>58–60</sup> The ionic resistance of the primers formulated with talc and zinc tetroxychromate was rather low. The ionic resistance of the films originated by the primers containing TT40 and LT40 as pigments increased continuously as time elapsed during the first hours, then dropped off to a final value that did not differ significantly from the other primers (Figure 7). The increased resistance could be explained by pore



**Figure 7.** Ionic resistance of primed panels with TT40 or its derivative LT40, as a function of time, in 0.1 M NaCl.

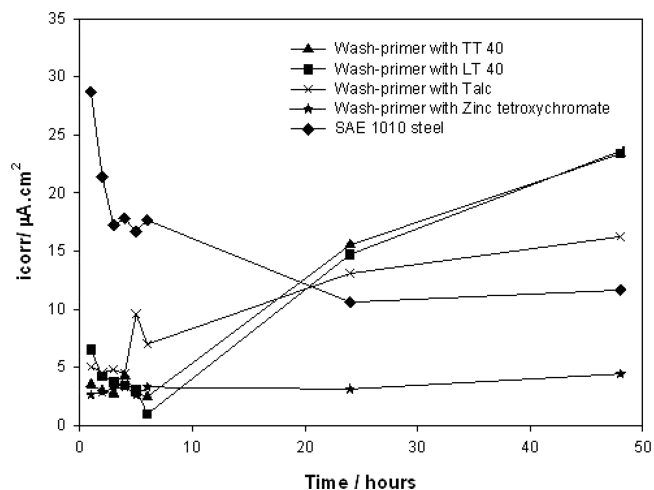
plugging due to corrosion products. It may be observed that the ionic resistance of the primers formulated with TT40 and LT40 is ten times higher than that of the primers containing TT80 and LT80. This fact would foresee better barrier properties in the first case (Figures 7 and 8).

The primer containing ZTC was the most effective in reducing the corrosion rate of steel (*icorr*). *icorr* did not change significantly along the test. Initially, steel corrosion rate of the panels coated with the rest of the primers was greater than that of the ZTC primer. After 3 h of immersion steel corrosion rate of all primed panels was similar to each other. The corrosion rate of these primers began to increase after 5 h; it continued increasing until the end of the test period. Steel corrosion rate for the primers pigmented with TT40 and LT40 were similar

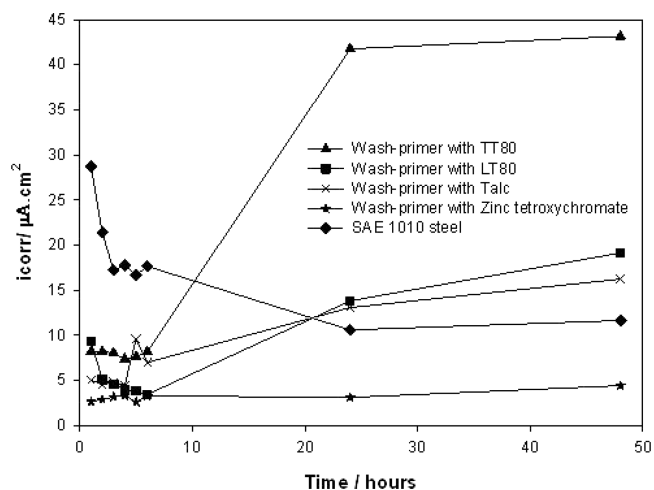


**Figure 8.** Ionic resistance of primed panels with TT80 or its derivative LT80, as a function of time, in 0.1 M NaCl.

while LT80 had better anticorrosive performance than TT80 (Figures 9 and 10).

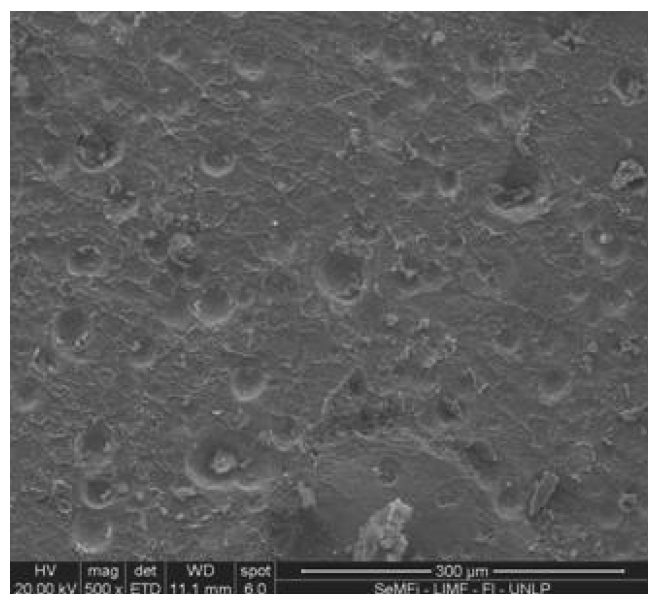


**Figure 9.** Corrosion rate of primed panels formulated with TT40 and LT40, as a function of time, in 0.1 M NaCl.

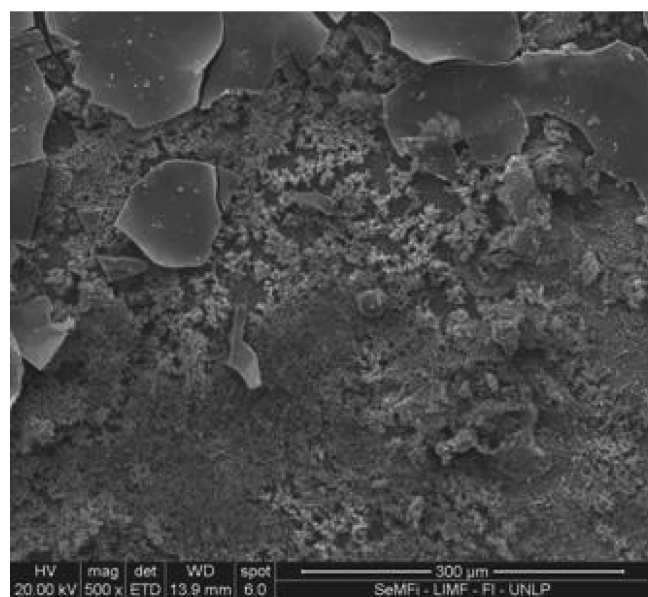


**Figure 10.** Corrosion rate of primed panels formulated with TT80 and LT80, as a function of time, in 0.1 M NaCl.

After SEM examination, the steel surface in DW seemed to be covered with an oxide layer partially destroyed by pitting (Figure 11a). The surface morphology was modified in both



a



b

**Figure 11.** Steel surface morphology after 24 h of exposure: (a) in the supporting electrolyte, (b) TT40 suspension, (c) in TT80 suspension, (d) in LT40 suspension, (e) in LT80 suspension.

TT40 and TT80 suspensions. In the case of TT40 the protective film contained plates and powdery formations typical of tannins (Figure 11b).<sup>61</sup> Pits were not detected (Figure 11b). The surface in contact with TT80 was quite different and many globular oxide formations could be observed. Pits were not observed, they may be covered with iron oxides (Figure 11c). The surface morphology in LT suspensions changed significantly. A very thin film covered the steel surface (Figure 11d and e). It was considered that the protective film is thin

because the polishing lines could be seen in both cases. According the surface elemental analysis both film contained C, probably due to the formation of a tannate coating. The content of La was very high in the case of the steel panel in contact with the LT40 suspension and nondetectable for the panel in the other suspension (Table 2).

**Table 2.** Lanthanum Tannate Film Composition after EDS Spectrum

%Wt	C	O	La	Fe
LT40	13.4	14.4	31.9	40.3
LT80	5.71	0.49	nondetectable	93.8

**3.3. The Behavior of the Wash-Primer in a Paint System.** After one and a half month of exposure, results in the accelerated tests (salt spray and humidity chambers) showed that all wash-primers had similar anticorrosion behavior than the primer formulated with ZTC.

In the salt spray chamber, the primer formulated with talc begun to fail after 52 days of exposure (SI Table S2). At longer exposure time (90 days), the primer containing LT40 (qualification 8P) performed similar to the one formulated with ZTC (qualification 9P). The primers formulated with both tannins exhibited a slightly worse behavior than those pigmented with LT40.

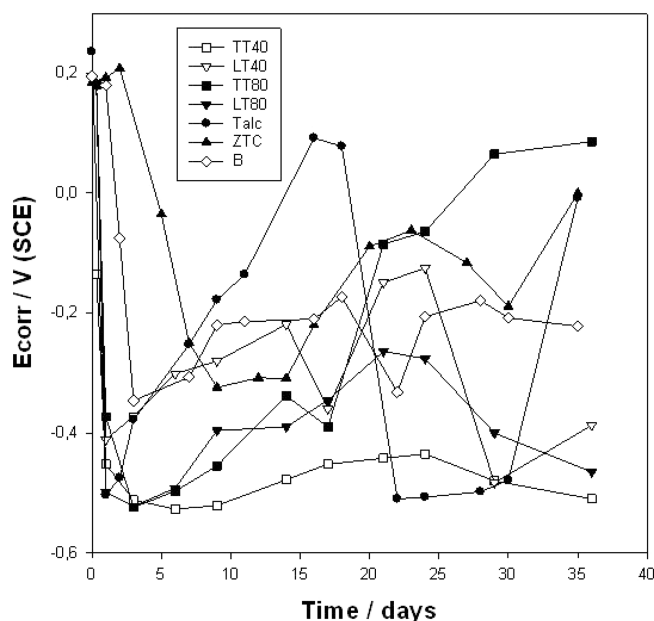
Alkyd systems are prone to fail by blistering in the humidity chamber. All tested paints blistered after the first day of exposure (SI Table S3). Blistering did not change significantly in the case of the primers containing either tannins or tannates. Blistering was intense in the case of the primer containing ZTC and talc; the panels coated with these formulations were removed from the chamber after 31 days of exposure.

As a trend, the corrosion potential of painted panels was displaced to more positive values with respect to the steel corrosion potential ( $E_{\text{corr}} = -0.650$  V, Figure 12); particularly, at the beginning of the exposure time. The oscillating behavior was attributed to active-passive transitions.

As an example, Bode's plots corresponding to the painting schemes containing the primer formulated with TT40 and that pigmented with LT40 are shown in Figure 13a and b, respectively. The simple observation of these plots revealed that one or two time constants may appear depending on the exposure time.

Impedance data were fitted using equivalent circuits as those depicted in Figure 14, previously discussed in the literature.<sup>62,63</sup> The first one, with only one time constant, describes the film properties. The second one was employed to fit experimental data once the corrosion process was started. The exact number of time constants was determined from the fitting of experimental data, according to the point of view adopted by Amirudin and Thierry.<sup>62</sup>

Distortions observed in the resistive-capacitive contributions indicate a deviation from the theoretical models due to either lateral penetration of the electrolyte at the steel/paint interface (usually started at the base of intrinsic or artificial coating defects), underlying steel surface heterogeneity (topological, chemical composition, surface energy) and/or diffusional processes that could take place along the test. Since all these factors cause the impedance/frequency relationship to be nonlinear, they are taken into consideration by replacing the capacitive components ( $C_i$ ) of the equivalent circuit transfer function by the corresponding constant phase element  $Q_i$



**Figure 12.** Corrosion potential of steel panels coated with the different painting schemes.

(CPE), thus obtaining a better fit of data. The CPE is defined by the following equation:<sup>64</sup>

$$Z = \frac{(j\omega)^{-n}}{Y_0}$$

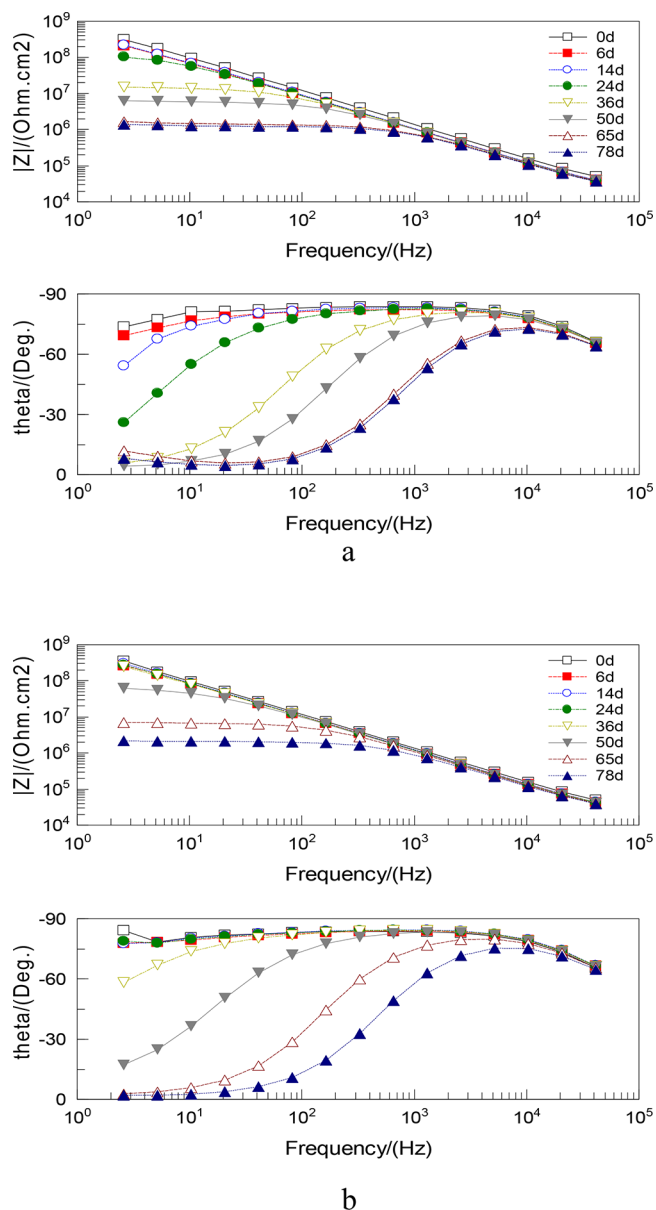
where  $Z \Rightarrow$  impedance of the CPE ( $Z = Z' + Z''$ ). ( $\Omega$ ),  $j \Rightarrow$  imaginary number ( $j^2 = -1$ ),  $\omega \Rightarrow$  angular frequency. (rad),  $n \Rightarrow$  CPE power ( $n = \alpha/(\pi/2)$ ). (dimensionless),  $\alpha \Rightarrow$  constant phase angle of the CPE. (rad),  $Y_0 \Rightarrow$  part of the CPE independent of the frequency. ( $\Omega^{-1}$ ).

The accuracy of the fitting procedure was measured by the  $\chi^2$  parameter obtained from the difference between experimental and fitted data; the most probable circuit was selected providing that  $\chi^2 < 10^{-4}$ .

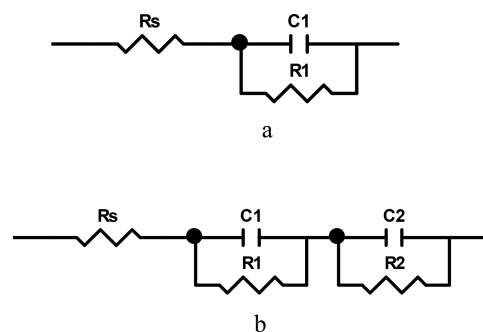
In the present work, the fitting process was mainly performed using the phase constant element  $Q_i$  instead of the dielectric capacitance  $C_i$ . However, this last parameter was used in the plots in order to facilitate results visualization and interpretation. As an example, the result of the fitting process, corresponding to one paint scheme and one and two time constants is presented in SI Figure S2.

The barrier properties of the painting scheme depended on the alkyd paints because the ionic resistance of the primers was low (Figure 15). All the paint systems tested showed a full barrier to ion diffusion at the beginning of the immersion period as it could be deduced from the pore resistance ( $R_1$ ) values which were higher than  $1.0 \times 10^8 \Omega \cdot \text{cm}^2$ ; the threshold value suggested in the literature.<sup>65,66</sup> The exception was the painting scheme without primer (Figure 15a, blank). Afterward, all the paint systems maintained a residual protection ( $10^6 \Omega \cdot \text{cm}^2 < R_1 < 10^8 \Omega \cdot \text{cm}^2$ ) except that formulated with LT80 (Figure 15b). The differences observed among the different paint systems could be attributed to different interactions between each coating.  $R_1$  oscillations, as time elapsed, could be explained by the pore plugging-unplugging due to corrosion products.

The highest value of the charge transfer resistance ( $R_2$ ) was obtained for the paint system containing the wash-primer



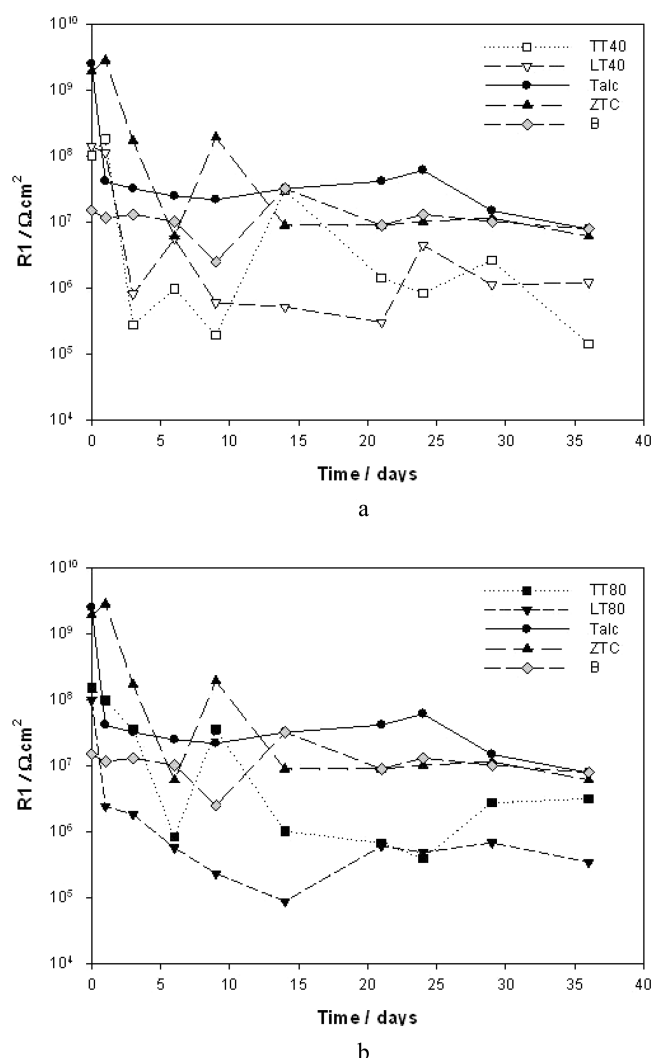
**Figure 13.** Bode's plots: (a) painting scheme containing the wash-primer pigmented with TT40; (b) painting scheme containing the wash-primer pigmented with LT40.



**Figure 14.** Equivalent circuits employed to fit experimental data.

pigmented with ZTC. However, most of all the measured values were comprised between  $10^7$ – $10^8 \Omega \cdot \text{cm}^2$ , at least during the first 3 weeks of immersion; thus revealing that these systems could also protect steel from corrosion. As a trend, the



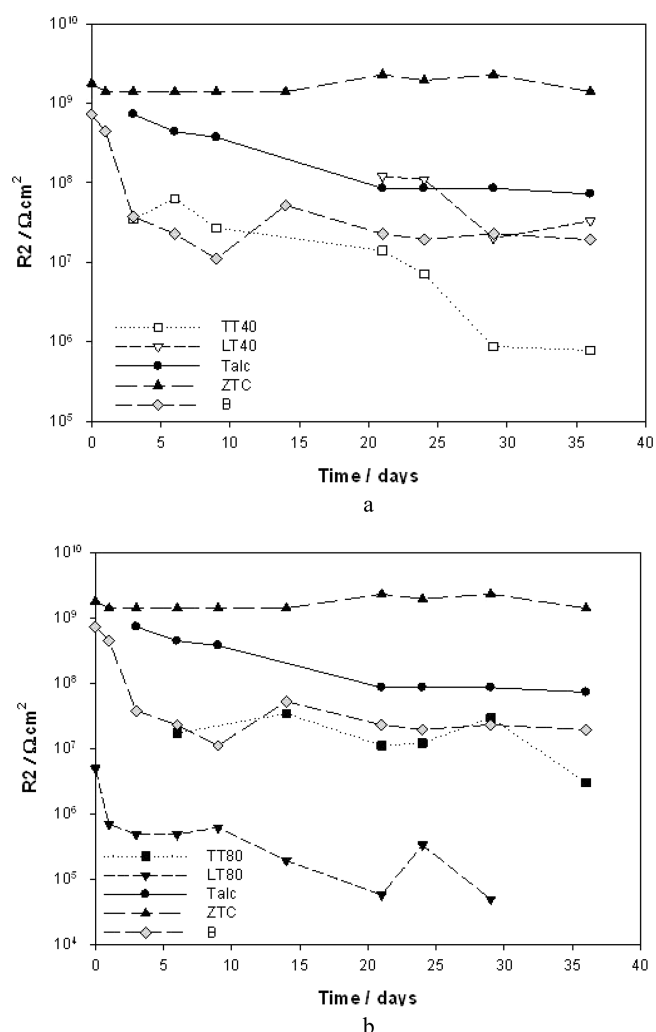


**Figure 15.** Pore resistance of steel panels coated with the different painting schemes: (a) TT40 and its derivative LT40; (b) TT80 and its derivative LT80.

charge transfer resistance of the systems with a wash-primer was higher than that of the control, thus increasing the resistance of the coated metal to corrosion (Figure 16a and b). It must be pointed out that the corrosion process was delayed in some cases which was evidenced by the absence of the R2C2 time constant in certain periods of time, particularly at the beginning of the immersion time. The corrosion process was delayed 3 weeks in the case of the primer containing LT40 while it was detected from the very beginning of the test period in the case of the wash-primer formulated with ZTC.

The values of the film capacitance ( $C_1$ ) pointed out that all tested systems showed an incipient loss of integrity ( $C_1 > 10^{-9} \text{ Fcm}^{-2}$ , Figure 17a and b). The best behavior was observed for the paint system with the primers containing either ZTC or talc.

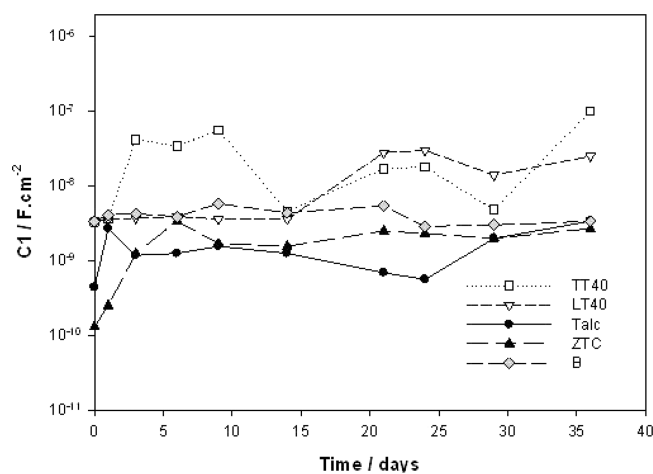
The capacitance of the double layer ( $C_2$ ) was almost 2 orders of magnitude lower for the systems containing the different wash-primer (Figure 18a and b). There are no significant differences between the tested paint systems containing a wash-primer. The presence of these primers in the paint system reduced the electrochemical active area.



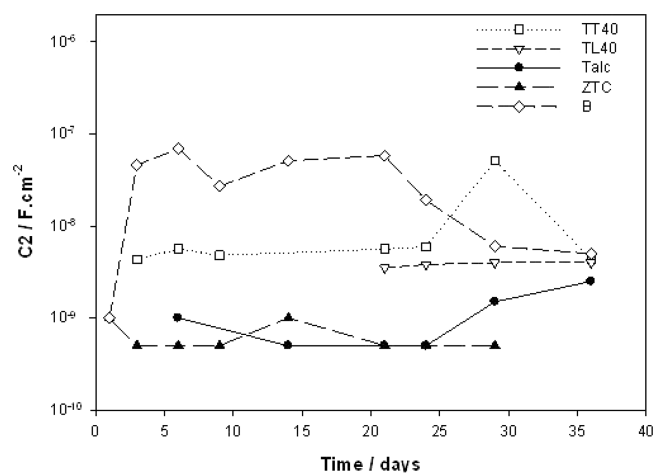
**Figure 16.** Charge transfer resistance of steel panels coated with the different painting schemes: (a) TT40 and its derivative LT40; (b) TT80 and its derivative LT80.

## CONCLUSIONS

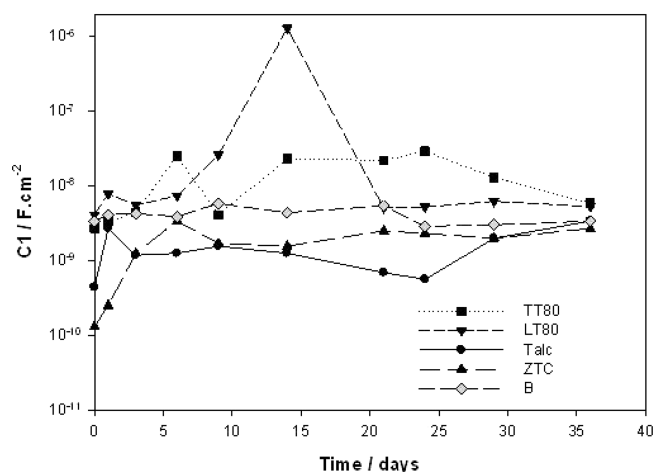
1. The optimum relationship mmoles  $\text{La}(\text{NO}_3)_3/\text{mass}$  of Tara tannin to precipitate the lanthanum tannate was 3 mmol/0.50 g at pH 8. Tara tannins were completely precipitated at pH 8 as it could be deduced from the solubility of both lanthanum tannates.
2. Both lanthanum tannate (LT40 and LT80) can act as a reservoir of  $\text{La}(\text{III})$  due to their content of  $\text{La}(\text{III})$  (26.0% for LT40 and 28.0% for LT80, respectively).
3. Tara tannin solutions could be more aggressive than the supporting electrolyte taking into account the pH 3 of their suspensions. In change, steel corrosion was highly reduced in the corresponding tannate suspensions.
4. After 3 h of immersion, steel corrosion rate of all primed panels did not differ significantly from each other. At longer exposure times, the primer containing zinc tetroxychromate (ZTC) was the most effective in reducing the corrosion rate of steel.
5. Steel surface morphology was modified in Tara tannins (TT40 and TT80) suspensions. The oxide layer, partially destroyed by pitting, was replaced by a film which contained plates and powdery formations typical of tannins. Pits were not detected in the presence of



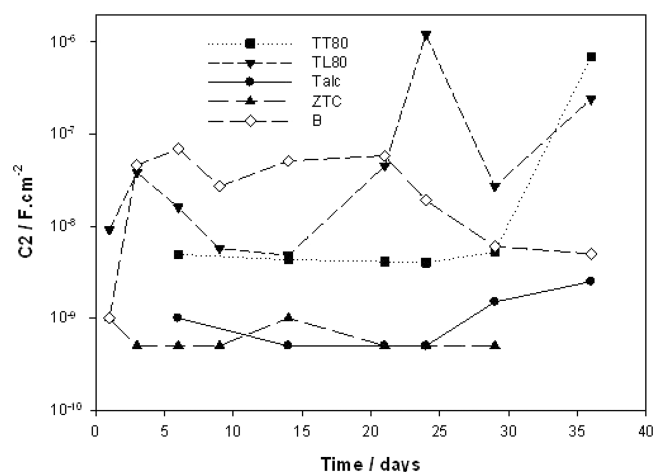
a



a



b



b

**Figure 17.** Coating capacitance of steel panels coated with the different painting schemes: (a) TT40 and its derivative LT40; (b) TT80 and its derivative LT80.

**Figure 18.** Double layer capacitance of steel panels coated with the different painting schemes: (a) TT40 and its derivative LT40; (b) TT80 and its derivative LT80.

tannins. TT80 was less efficient than TT40 on protecting steel. The surface morphology in lanthanum tannate suspensions was also different and a very thin film covered the steel surface. The content of La on the surface was very high in the case of the steel panel in contact with the LT40 and this fact is responsible of its improved anticorrosion performance.

- The anticorrosion performance of the primers improved when they were incorporated into a complete painting scheme.
- Accelerated tests performed on painted panels revealed that at longer exposure time (90 days) the primer formulated with LT40 performed as the one containing ZTC. The primers formulated with both tannins exhibited a slightly worse behavior than those pigmented with LT40.
- The highest value of the charge transfer resistance was obtained for the paint system containing the wash-primer pigmented with ZTC. However, the corrosion process was delayed for a long period in the case of the primer containing LT40. This fact points out that the primer pigmented with LT40 could be employed satisfactorily instead of that formulated with ZTC. The charge transfer

resistance values of the rest of the primers suggest that they also could be employed as temporary corrosion protective coatings.

- The presence of a wash-primer in the paint system reduced the electrochemical active area.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.iecr.7b03317](https://doi.org/10.1021/acs.iecr.7b03317).

Table S1: SAE 1010 steel corrosion rate in tannins and tannins derivatives suspensions in 0.10 M NaCl. Table S2: Rusting degree (ASTM D610) of painted panels exposed in the salt spray chamber (ASTM B117). Table S3: Blistering degree (ASTM D714) of painted panels exposed in the humidity chamber (ASTM D2247). Figure S1: Polarization curves of "Tara" tannins (2 ppm) and lanthanum "tannates". The electrolyte used was 0.1 M NaCl, the scan rate was 0.5 mV.s<sup>-1</sup> and the exposure time was 2 h. Figure S2: Experimental data and fitting curves of steel panel coated with the painting scheme containing the primer formulated with TT40 a) just after

immersion (one time constant), b) after 78 days of immersion (two time constants) (PDF)

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### Notes

The authors declare no competing financial interest.

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