Formulation and Testing of a Waterborne Primer Containing Chestnut Tannin

O.R. Pardini, J.I. Amalvy, A.R. Di Sarli, R. Romagnoli, V.F. Vetere—Centro de Investigación y Desarrollo en Tecnología de Pinturas* (CIDEPINT)

The development of a water-based pretreatment system containing chestnut tannin and phosphoric acid and the assessment of its anticorrosive properties through different conventional tests are discussed in this work. Treated steel panels coated with different paint systems were subjected to standardized (salt spray, humidity chamber, adhesion, and flexibility) and electrochemical (corrosion potential, EIS) tests. Electrochemical tests were performed by employing only panels coated with the wash primer to determine its protective effect. The binder employed in this research was prepared in the laboratory by emulsion polymerization of acrylic monomers.

It was found that the tested formulation protected steel against corrosion by forming ferric tannate, which prevented oxide formation. After performing the salt spray tests, it was observed that no oxide spots developed on the scratch mark, although some blisters were detected. The good stability of the binder in low pH media (pH: 2.0-2.5) and the binder/substrate interaction are decisive factors in the performance of this aqueous pretreatment system.

INTRODUCTION

Wash primers designed to protect steel structures against corrosion normally contain chromates. Because of their toxicity, chromates constitute a hazard and need to be replaced by more environmentally acceptable corrosion inhibitors. In this sense, tannins, a class of natural, non-toxic, biodegradable organic compounds, are being proposed as an alternative in primary painting systems.

Tannins are polyphenols of vegetal origin and the proximity of hydroxyl groups on the aromatic rings makes them able to chelate iron ions. Ferric tannates of dark blue color are highly insoluble and act as electric insulators between cathodic and anodic sites on the metal surface.[1-8]

The formation of iron tannates was studied by Ross and Francis by infrared spectroscopy.[7] Tannins showed a very broad absorption band between 3,700 and 2,700 cm^{-1} due to the presence of hydroxyl groups. Three peaks occurred at 1,600, 1,500 and 1,450 cm^{-1}, which are characteristic of aromatic compounds. Various peaks in the 600 to 900 cm^{-1} region and smaller peaks between 1,000 and 1,200 cm^{-1} are characteristics of substituted benzene rings. The spectrum corresponding to products resulting from the reaction between iron compounds and tannin showed a similar pattern, although resolution was not as good. The major difference was in the OH region where absorption was much less, thus indicating that the hydroxyl bonds had been weakened as would occur after the chelation with iron ions.

Seavell[4] demonstrated that small amounts of iron, approximately 2.5%, are bonded to tannins in ferric tannate. Vetere et al.[2] found that this amount may vary with the type of tannin employed to precipitate ferric tannate and with the pH of the medium. At a pH of 4, chestnut tannin precipitated on an average of 700 mg of tannin per 56 mg of ferric cation, while for other tannins such as "quebracho" and mimosa, 500 mg of tannins reacted with 56 mg of ferric cation.

Tannins as corrosion inhibitors are applied both in solvent and in waterborne pretreatment formulations. These formulations could be applied on partially rusted substrates, reducing the effort needed for cleaning the surface by sandblasting or other methods.[7,9] They have been called rust converters since their presence converts active rust into iron tannates, which do not further react with corrosive agents and impede steel corrosion.

*Av. 52 entre 121 y 122, (1900) La Plata, Argentina; Tel. 54-221-4831141/44. Fax 54-221-4271537. email: cidepint@ba.net

Table 1—Raw Materials Employed in Latex Synthesis

Reagents	Initial Load (g)	Feed (g)
Ethyl acrylate	220.00	—
Methyl methacrylate	75.65	144.35
Ethylene glycol dimethacrylate	0.29	0.15
Methacrylic acid	—	8.80
Potassium persulfate	2.74	—
Sodium lauryl sulfate	2.96	1.53
Distilled water	355.65	53.15

The anticorrosive behavior of steel panels treated with solvent-based formulations and coated with alkyd, vinyl, and epoxy paint systems (anticorrosive paint plus a topcoat, final thickness between 70 and 150 μm), was assessed employing accelerated tests and electrochemical techniques. Untreated steel panels coated with the same paint systems were used as blanks. It was shown that paint adhesion and anticorrosive properties of the paint systems were improved when they were applied in combination with pretreatment formulations containing tannins. No blistering was observed up to 500 hr of exposure to the salt spray test; blisters began to develop after 1,000 hr of exposure.[10-12] The presence of the primer delayed the onset of corrosion for 150-250 hr, with the length of the delay dependent on the type of binder employed. Epoxy paints proved to be the most resistant to corrosion.[11] The system can be used on clean or slightly rusted surfaces of variable roughness; although better results were reported to be obtained with slightly rusted surfaces (oxide layer < 100 μm thick).[7,10-12]

The pretreatments containing tannins reduced the steel corrosion rate by a factor of two to three with respect to conventional ones based on zinc chromate. The corrosion potential of pretreated panels was shifted at least +100 mV with respect to the corrosion potential of bare steel. The variation of the corrosion potential as a function of time, in an electrolytic solution, revealed a certain tendency of treated panels to repassivate.[10-12] The anticorrosive behavior depends not only on their composition but also on the barrier properties of the whole painting system.[1] Results of different tests showed that tannins could not be employed alone and, in the case of exposure to severe conditions, the incorporation of an anticorrosive paint in the painting system is mandatory.[1,2,10-12]

The reaction mechanism of tannins added to primary paints for steel protection is not well understood, and their efficiency is questioned by some authors.[1,3,4] Tannin penetrates the rust to varying depths and, usually, half of the rust is affected by the pretreatment system. The reaction of tannins with iron compounds yields to the formation of iron tannates, as stated previously. However, some authors have reported the formation of magnetite, an adherent and protective oxide, as a consequence of the reduction of ferric ions to ferrous ones by tannins.[7,8] Faure and Landolt[5] stated that magnetite could not be formed in the presence of gallic acid or tannins. These compounds chelate iron ion to form a precipitate, which insulates cathodic and anodic areas preventing the chemical reaction between ferrous and ferric compounds and forming magnetite. It seems that some magnetite could be formed after two to three months' exposure if some ferrous tannate was trapped in the film after drying and deprived of oxygen. After three months, oxidation was reported to begin again, with lepidocrocite being the final oxidation product.[3,7]

Table 2—Tested Painting Systems

System	Tannin Pretreatment	Anticorrosive Paint	Topcoat
1	Yes	—	60 μm
2	Yes	60 μm	—
3	Yes	30 μm	30 μm
4	—	35 μm	35 μm

NOTES:
In all cases wash coat film thickness was 10 ± 2 μm.
Anticorrosive paint was an alkyd pigmented with "zinc molybdenum phosphate" (30% by volume) and with a PVC/CPVC ratio equal to 0.8.
Topcoat was alkyd paint pigmented with titanium oxide.

The influence of phosphoric acid on the performance of these systems has also been studied. The transformation of rust by phosphoric acid depends strongly on the concentration of the acid. It is only above 8 M concentration that ferric phosphate is formed. Below this concentration level, the transformation is dependant on the initial corroding medium. In most cases β- and γ-FeOOH and ferrihydrite are likely to be formed.[15,16]

Little information concerning the preparation and performance of aqueous pretreatment systems containing tannins was found in the literature.[12,17,18] These systems seem to perform in a similar way to the solventborne ones. Formulations containing phosphoric acid, without incorporating tannins, have also been developed. In this sense, a single-step phosphate/paint system composed by polyester-melamine enamels and phosphoric acid was formulated successfully.[19] Phosphoric acid was found to migrate and react with the surface of the steel panel. This resulted in the formation of metal phosphates such as $Fe(H_2PO_4)_2$, $FeHPO_4$, $Fe_3(PO_4)_2$, $FePO_4$, etc. These compounds are thought to passivate the substrate and provide the proper functionalities for the condensation reactions with binders.

It is the aim of this research to formulate a water-based anticorrosive pretreatment system and determine its anticorrosive performance through mechanical, chemical, and electrochemical evaluations. The synthesis of the binder was carried out in the laboratory in order to achieve a well-defined formulation compatible with the characteristic acidity of this type of product.

EXPERIMENTAL

Pretreatment System Formulation and Application

Binder: The film forming material was an all-acrylic emulsion prepared in the laboratory by semicontinuous emulsion polymerization.[20,21] An acrylic resin was selected because it is of low cost, easy to prepare in the laboratory, and has the possibility of being compatible with phosphoric acid. Moreover, this resin, as it will be pointed out later, did not coagulate in the presence of tannins.

Analytical grade monomers (Fluka Chemika®) were used as received. Methyl methacrylate (MMA) contained 25 ppm of hydroquinone. Ethylene glycol dimethacrylate (EGDMA), ethyl acrylate (EA), and methacrylic acid (MAA) contained hydroquinone monomethyl ether, 50, 100, and 200 ppm, respectively. The emulsifier, sodium lauryl sulfate (SLS), and the initiator, potassium persulphate (KPS), were of analytical grade and were used without further purification. Distilled water (DW) was used throughout the binder synthesis.

Polymerizations were carried out using a two-piece reactor composed of a conical-based glass vessel (capacity 1.30 dm^3, with a thermostatic jacket and sampling utility) and a five-necked cap. The cap was fitted with a reflux condenser, a stirrer (Teflon® two-blade propeller type), an inlet for inert gas (nitrogen), a thermocouple, and an inlet for the pump. The agitation speed was about 200 rpm. The list of latex components is given in *Table* 1.

The procedure for emulsion polymerization was as follows: the initial SLS was added to the water in the reactor followed by the addition of all the EA (the less reactive monomer) and the initial load of MMA and EGMA, as indicated in *Table* 1, with stirring. Nitrogen was passed through the emulsion for 30 min while heating up to 60°C. The initiator was dissolved in 30 mL of DW, preheated (60°C), and then poured into the reactor chamber. The emulsion was allowed to react for ca. 15 min, during which time in situ seed particles were formed; then the feed was started at ca. 2 g of emulsion per minute. The emulsion flow rate was adequately adjusted to add the MAA in the last part of the reaction together with the remaining reactants. An emulsification apparatus was used to prepare the monomer emulsion by stirring at 1,500 rpm. The emulsion was then placed in a dropping funnel and deaerated for 30 min.

After monomer addition, the temperature was maintained at 80°C for ca. 120 min to complete polymerization. The latex solid content was measured gravimetrically by taking a few grams sample from the reactor and drying it under reduced pressure at 50°C.

Particle size was estimated by spectroturbidimetry,[22] and the glass transition temperature (T_g) was calculated using Fox's equation.[23] Surface tension was measured by means of the Du Noüy tensiometer.[24] More experimental details on binder characterization are given in a previous paper.[21]

Tannin: Chestnut tannin was selected because it is more reactive than mimosa and quebracho tannins; it also exhibits the highest reaction rate with steel.[2]

Pretreatment Manufacture and Application: Typical preparation is according to the following process (patent pending): 10 mL of a phosphoric acid solution (30% by weight) was added to a 6 g suspension of chestnut tannin in 40 mL of distilled water and heated at 100°C for half an hour. During this operation, tannin combined with phosphoric acid through a chemical reaction yielding a product more acidic than phosphoric acid itself. This association compound enhanced the adhesive strength of tannin on steel.[25] The acid constant of this product, K_a, was determined by potentiometric measurements according to a well-known analytical procedure[26] and compared with the acid constant of phosphoric acid.

The treated tannin was cooled and filtered to eliminate insoluble matter (approximately 2-5% in the case of chestnut tannin) and mixed with a 40% aqueous solution of the acrylic binder, prepared as described, plus 2 mL of Texanol® and a flash rusting inhibitor.[25] In this case, 3 mL of 10% solution of ammonium molybdate was employed as a flash rusting inhibitor. The system was allowed to stand for 24 hr and filtered off again, if necessary, to remove insoluble material.

The pretreatment formulation was brush applied on SAE 1010 steel panels (15.0 × 7.5 × 0.2 cm), which were previously degreased with toluene, up to a dry film thickness of 10±2 μm. Test panels had a low surface roughness (average value 0.78 μm and a valley to peak distance of 4.96 μm) and a slight oxidation. The low surface roughness was selected to perform the tests in an unfavorable condition with respect to the adherence of the first coat (pretreatment formulation containing tannin). Surface rugosity was measured employing a Hommel tester Model T1000 magnetic device.[27]

Panel oxidation was achieved by placing the panels in a chamber at 40±1°C and wetting them with distilled water perodically for two weeks. The oxide film thickness, measured by scanning electron microscopy in a cross sectional, averaged 100 μm. The oxide layer was FeOOH, and its morphology corresponded to amorphous iron oxide and lepidocrocite nests. Panels were brushed with a wire brush to remove weak and nonadhered corrosion products. The thickness of the remaining layer was 30 μm.[2]

The treated panels were kept in the laboratory atmosphere (RH 65±5% and 20±2°C) during seven days. Then, they were coated with different paint systems (*Table* 2) to perform accelerated tests because the pretreatment film alone cannot undergo them and was destroyed after one day of exposure.

The primer was formulated with a medium solventborne alkyd binder and contained zinc molybdenum phosphate; its anticorrosive performance was assessed in a previous research.[28] The topcoat was an alkyd paint containing 20% resin (the same employed for the anticorrosive paint), 20% titanium dioxide, and 60% solvent (white spirit). The solventborne coats were employed to make the painting system resistant to the salt fog test.

Laboratory Tests

Accelerated salt spray and humidity cabinet tests were carried out to evaluate corrosion and water resistance of painted panels. Mechanical tests, such as flexibility and adhesion, were also performed in order to get data related with the metal pretreatment interaction. Finally, the anticorrosive behavior was monitored by electrochemical impedance spectroscopy (EIS).

Salt Spray Test (ASTM B 117): A scratch line was made through the coating with a sharp instrument to expose the underlying metal to the aggressive environ-

Table 3—Latex Parameters

Parameter	
Solids content	47%
Mean particle diameter	144 nm
pH	2.0
Density	1.08 g cm^{-3}
Surface tension	31 mN m^{-1}
Glass transition temperature	35°C

ment.[29] After 400 hr of exposure, the panels were evaluated to establish the rusting degree[30] and failure at the scribe.[31] In all cases, tests were carried out in triplicate and the mean value of the results obtained in the test were reported. After visual examination, alkyd paints were removed by means of a hot five percent sodium hydroxide solution (65±5°C) to observe the pretreatment film with a Nikon binocular stereoscopic magnifier.

Humidity Cabinet Test (ASTM D 2247): Panels were exposed at 38±1°C for 250 hr[32] and the degree of blistering was evaluated according to current standard specification.[33] Afterwards, as was done in the case of the salt spray test, alkyd paints were removed, and the remaining film was subjected to microscopic examination.

Flexibility (ASTM D 522): The 3 mm mandrel was chosen to perform this test.[34]

Adhesion (ASTM D 4541): Adhesion measurements were carried out on treated panels and on panels covered with the painting systems mentioned in *Table* 2, according to ASTM D 4541 standard specification.[35]

Electrochemical Tests on Treated Steel Panels: These tests were performed on steel panels covered only with the primer to assess the anticorrosive action of the tannin primer by itself. In this sense, steel panels covered with the same primer composition but without tannin were also measured to discount the effect of the corrosion inhibitor. Cells to perform electrochemical measurements were constructed by fixing two acrylic tubes to the intact coated steel panel (working electrode) with an epoxy adhesive in order to get good adhesion. The geometrical area for each cell exposed to the electrolyte was 15.9 cm^2. A large area Pt-Rh mesh of negligible impedance and saturated calomel (SCE) was used as auxiliary and reference electrodes, respectively.

Each cell was filled up to a depth of 9 cm with a 0.5 M sodium perchlorate solution as the supporting electrolyte. Sodium perchlorate was chosen instead of sodium chloride, to delay the start of the steel corrosion process and make it possible to study the coating properties. The time of measurement was one week.

All impedance spectra in the frequency range 10^{-3}-10^5 Hz were performed in the potentiostatic mode at the corrosion potential as a function of the exposure time to the electrolyte solution using the 1255 Solartron FRA and the 1286 Solartron EI. The amplitude of the applied AC voltage was 10 mV peak to peak. Data processing was accomplished using the program developed by Boukamp[36] and a set of equivalent electrical circuits reported elsewhere.[37]

RESULTS AND DISCUSSION

Binder: The acid binder employed in this research had 47.7% of solids and an average particle diameter of 144 nm. The complete set of latex parameters is summarized in *Table* 3.

Pretreatment Manufacture and Application: The acid constant of the product obtained by reaction between tannin and phosphoric acid was found to be equal to 4.0×10^{-2} while the first acidic constant for phosphoric acid is 7.0×10^{-3}. The good colloidal stability of the primer, at low pH values (2.0-2.5), was attributed to a combined stabilization mechanism of the sulphate from

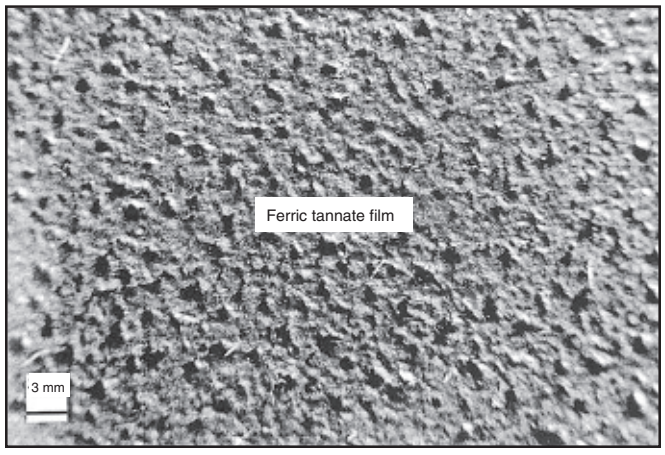

Figure 1— Micrograph (3.3X) of the ferric tannate film, after 400 hr exposure in the salt spray test, of a treated panel covered with an anticorrosive paint plus a topcoat (system 3, Table 2), after removal of alkyd coats. Scale: 1.0 cm = 3.3 cm.

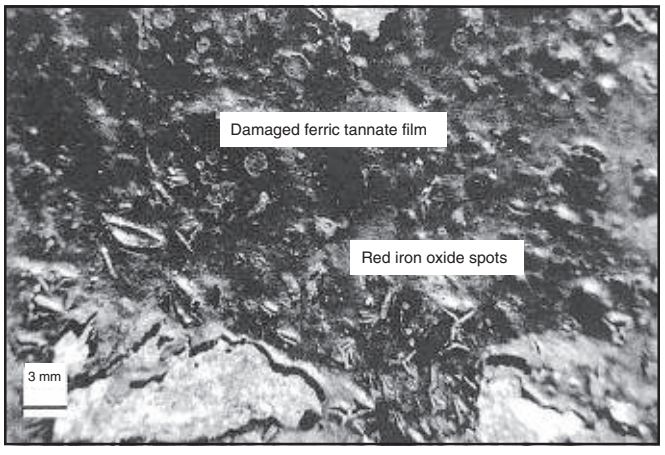

Figure 2—Micrograph (3.3X) of the ferric tannate film, after 400 hr exposure in the salt spray test, of a treated panel covered with an anticorrosive paint without a topcoat (system 2, Table 2), after removal of alkyd coat. Scale: 1.0 cm = 3.3 cm.

surfactant and the carboxylic groups from methacrylic acid.

Once the pretreatment system was applied on steel, the surface turned quickly to a black color because of the formation of an association compound known as iron tannate.[2,4,7] The tannate is actually formed by chelation of ferric cations coming either from the oxide or steel dissolution as a consequence of the pretreatment acidity. The presence of iron tannate was confirmed by FTIR spectrometry by assigning the characteristic peaks of the spectrum according to data reported in the literature.[2,7]

To conduct accelerated and adherence tests, different systems were applied (*Table* 2) on this black iron tannate-acrylic resin film.

Salt Spray Test (ASTM B 117): Steel panels coated only with the pretreatment film without topcoating were tested but failed in the unscribed area after one day of exposure.

Regardless of the zones adjacent to the scratch mark, the paint systems numbered 1, 3, and 4 in *Table* 2 showed good behavior after 400 hr exposure (qualification ≥ 8, i.e., 0.1% of the surface became rusted[29]). On the other hand, system 2 exhibited poor anticorrosive performance after 400 hr (qualification = 3, i.e., 16% of the surface rusted[29]) due to the higher permeability of the anticorrosive primer (pigment volume concentration, PVC, 0.40) with respect to the topcoat (PVC, 0.25). Failure began after 250 hr exposure (*Table* 4).

Microscopic examination (3.3×), performed after removing the alkyd paints, revealed that the pretreatment film remained undamaged in the coated panel corresponding to system 3 (*Figure* 1). Some cracks were formed in certain regions, probably during the film re-drying process which occurred after the test was performed and the alkyd paint was removed. However, no corrosion signs on the base metal were observed at the bottom of the cracks. The absence either of anticorrosive primer (system 1) or topcoat (system 2) led to a partial damage of the wash primer and underfilm oxide growth (*Figure* 2). Although panels coated with the anticorrosive primer and the topcoat (system 4) obtained a good qualification after this test, the removal of the paint revealed the presence of red iron oxide spots on the substrate.

Treated panels (systems 1, 2, and 3) developed blisters in the zone adjacent to the scratch mark due to the loss of adherence between the pretreatment and the alkyd paint. Despite the corrosion process being more intense in this zone, not much oxide was observed in the scratch line because it was incorporated into the pretreatment film, which changed color from black to red (*Figure* 3). Failure at the scribe was diminished by the presence of the complete paint system (*Table* 4).

According to results shown in *Table* 4, the performance of the paint system is mainly determined by the topcoat paint, although it seemed that the presence of the complete paint system (system 3) improved anticorrosive behavior. These results are in accordance with the fact that tannin pretreatments must be employed in complete paint systems when subjected to severe exposures.[1,4]

Humidity Cabinet Test (ASTM D 2247): As a general rule, it was observed that in all samples blisters developed during the first three days of exposure. After this period, no significant increase in blister size or blister surface density was observed (*Table* 4). When blisters

Table 4—Blistering for Tested Painting Systems after 250 hr Exposure in the Humidity Chamber Rusting Degree, and Failure at the Scribe for Tested Painting Systems, after 400 hr Exposure in the Salt Fog Chamber (ASTM B 117-90)

System	Rusting Degree in the Salt Fog Chamber (ASTM D 610-85)	Failure at the Scribe (ASTM D 1654-92)	Blistering in the Humidity Chamber (ASTM D 714-87)
1	8	7	8M*
2	3	5	8M*
3	9	9	6MD*
4	9	8	8F*

* M: medium; MD: medium dense; F: few

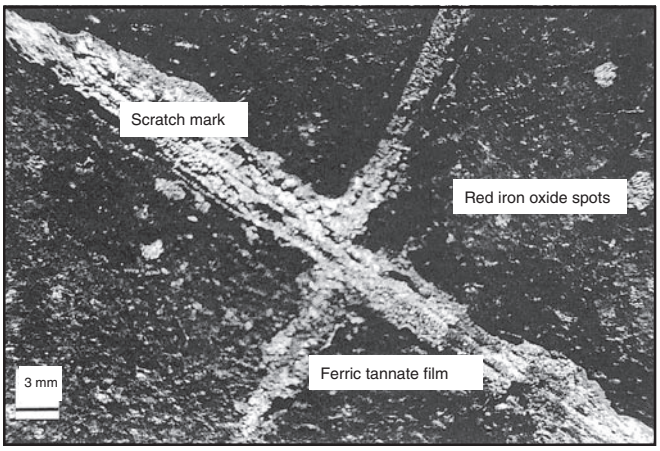

Figure 3— Micrograph (3.3X) of the ferric tannate film at the scratch mark, after 400 hr exposure in the salt spray test, of a treated panel covered with an anticorrosive paint plus a topcoat (system 3, Table 2), after removal of alkyd coats. Scale: 1.0 cm = 3.3 cm.

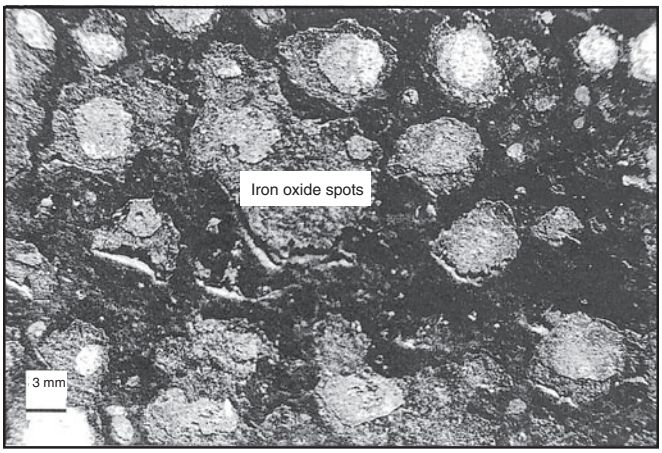

Figure 4—Micrograph (3.3X) of the ferric tannate film, after 250 hr exposure in the humidity chamber, of a treated panel covered with an anticorrosive paint without a topcoat (system 2, Table 2), after removal of alkyd coat. Scale: 1.0 cm = 3.3 cm.

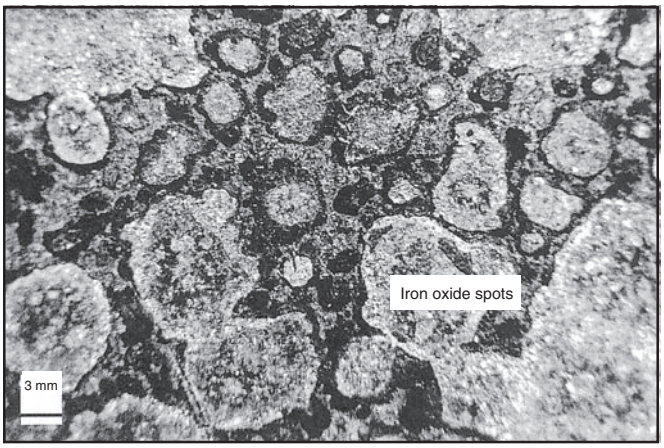

Figure 5—Micrograph (3.3X) of the steel surface, after 250 hr exposure in the humidity chamber, of a panel covered with an anticorrosive paint plus a topcoat (system 4, Table 2), after removal of alkyd coats. Scale: 1.0 cm = 3.3 cm.

were carefully broken with the aid of a needle and the stereoscopic magnifier at the end of the test, it was noticed that the loss of adherence had taken place first at the pretreatment film/anticorrosive paint interface and then at the steel/pretreatment film interface. No corrosion products were observed in the delaminated areas in the case of system 3. The higher blistering observed in system 3 may be attributed to the presence of the complete paint system which obstructed the escape of water from the film. The absence of either anticorrosive paint (system 1) or topcoat (system 2) in the system led to film destruction and oxide growth, as can be seen in *Figure* 4, that corresponds to system 2. Pretreatment film absence also led to oxide development (*Figure* 5).

Flexibility by Mandrel Bend Test Method (ASTM D 522): The primer containing tannin behaved satisfactorily in this test and no cracks were observed within the film after bending.

In the case of the alkyd paints, it was noticed that some cracking had occured after performing the test, which was attributed to certain incompatibility between the primer and the rest of the paint system.

Adhesion (ASTM D 4541-89): The average adhesion value obtained for panels covered with the primer alone are relatively high and equal to 20 ± 5 kg.cm^{-2} (*Table* 5). After performing this test it was observed that some ferric tannate remained firmly adhered on the steel surface, pointing out that metal pretreatment film interaction is responsible for the high adhesion values encountered. The values obtained in this test are lower in the case of complete paint systems (systems 2-4, *Table* 2). The failure occurred at the pretreatment/primer interface and it was noticed that film rupture left a thin white film from the anticorrosive coating on the black pretreatment.

Table 5—Adhesion (ASTM D 4541-89)

System	Adhesion (kg.cm^{-2})	Adhesion after the Salt Fog Chamber Exposure (kg.cm^{-2})
Pre-treatment system	20 ± 5	—
1	10	5
2	9	3
3	9	6
4	10	7

Adhesion was reduced after the salt fog chamber test; the failure zone was located at the intercoat zone between the pretreatment and the primer. As the adherence was reduced by the penetration of electrolyte solution, the system containing the anticorrosive primer (system 2, *Table* 2) showed the lowest values while the highest ones were observed for systems containing both the primer and the topcoat (systems 3 and 4, *Table* 2).

Electrochemical Tests on Treated Steel Panels: As stated previously, in order to confirm if the pretreatment had some anticorrosive properties, it was decided to study its electrochemical behavior independently of the complete paint system.

Corrosion potential measurements (*Figure* 6a) showed that the pretreatment protected the substrate because the corrosion potential remained more positive by +100 mV, compared to that of bare steel (~ –750 mV vs. SCE) after seven days of immersion. Pretreatment formulations without tannin are also said to have good anticorrosive properties.[38-40] However, it could be seen that corrosion potential of steel panels coated with a pretreatment without tannin decreased as a function of time and approached the value corresponding to bare steel in spite of containing the flash rusting inhibitor. The initial protection afforded with the tannin-free formulation may be attributed to the phosphoric acid, which by itself was not able to produce an effective phosphating of the steel surface, and protection was finally lost. White ferrous phosphate (vivianite) and some light brown ferric phosphate may appear on the steel surface treated with phosphoric acid. Obviously, these phosphates did not protect the metal substrate because the tannin-free pretreatment, which contained the same amount of phosphoric acid, did not achieve an efficient protection of the base metal. In the presence of tannin, these phosphates are readily converted into the more stable black ferric tannate,[2,4] which is thought to block the active sites for metal oxidation. In this sense, as shown later, the charge transfer resistance for the primer containing tannin was higher than that of the tannin-free pretreatment during the first day of immersion (*Figure* 6c).

A good description of the impedance spectra was attained through the transfer function analysis using non-linear fit routines. The painting system as well as the steel substrate deterioration took place according to complex processes. Consequently, to both interpret and explain the time dependence of the acquired impedance data, it was necessary to derive appropriate equivalent circuit models.[36] The relative performance of the coated steel under immersion conditions in 0.5 M sodium perchlorate solution was assessed by the variation of the resistive R_i and capacitive C_i components as a function of the exposure time.

Impedance spectra (*Figure* 6) provide important information concerning both the organic coating deterio-

ration and the kinetic of the corrosion process suffered by the underlying steel substrate. The resistance to ionic flux (R_f) is related to coating integrity; in this sense, values shown in *Figure* 6b indicate that the pretreatment films did not have a barrier effect to the electrolyte solution permeation towards the steel/paint interface. The slight increase of R_f at the end of the test period for the tannin-free primer may be due to pore sealing by corrosion products.[41]

The coating dielectric capacitance (C_f) values are associated with the amount of water permeating within and under the coating film. *Figure* 6d shows that the primer capacitance increased gradually, reaching values greater than those of the electrochemical double layer of bare steel in these media (i.e., when the coating protective properties are totally lost, the normal values fall between ~ 3-20 $\times 10^{-6}$ F.cm^{-2}). These abnormal values may be due to the great affinity of tannins and the binder for water.

As soon as the permeating corrosive species (water, oxygen, and ions) reach electrochemically active areas on the substrate, the steel corrosion process becomes measurable. Therefore, the electrochemical double layer capacitance (C_{dl}) and the charge transfer resistance (R_t) characterizing the faradaic process could be measured. In the present case, corrosion parameters were obtained from the very beginning of the test due to both the low thickness and the high permeability of the coating film. The charge transfer resistance for panels coated with the pretreatment containing tannin was higher than that of the free tannin one, and the double layer capacitance was lower indicating that the active area for the electrochemical reaction was smaller. In this sense, it was thought that the precipitated ferric tannate, acting together with the polymer of the binder, blocked more effectively the active sites on the metallic surface hindering the electrochemical reaction.[42] As time went on, the charge transfer resistance became slightly lower for the panel coated with the formulation containing tannin because tannins have a great affinity for iron ions to form ferric tannate, so steel corrosion increased.[2]

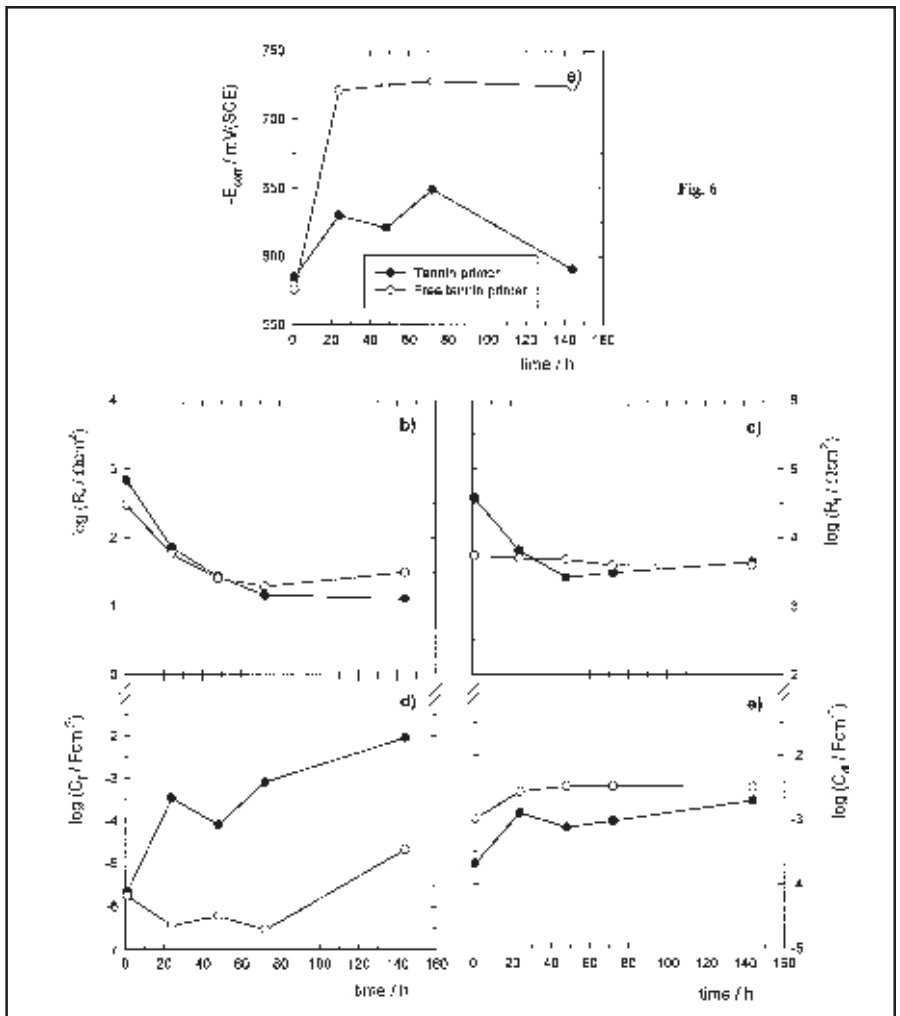

Figure 6—Time dependence of electrochemical parameters of the steel-primer interface: (a) corrosion potential, (b) ionic resistance, (c) primer dielectric capacitance, (d) charge transfer resistance, and (e) double layer capacitance. Electrolyte: 0.5 M sodium perchlorate solution.

CONCLUSIONS

(1) The pretreatment system containing tannin actually protects steel against corrosion, according to results from accelerated and electrochemical tests. However, to achieve a good anticorrosive protection in aggressive environments, an adequate painting system (anticorrosive + topcoat) must be applied.

(2) The pretreatment system with tannin, in combination with a complete paint system, also prevents the formation of oxide on the scratch mark.

(3) The pretreatment containing tannin adhered so strongly to the steel substrate that adhesion failure in complete painting systems took place at the primer/alkyd system interface.

(4) Tannins react with a ferric cation to yield an iron association compound ("ferric tannate"), which in combination with the polymer gives a film that inhibits further oxidation of the base metal by a kinetic hindering mechanism.

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