

FORMULATION AND TESTING OF A WATER-BORNE PRIMER CONTAINING CHESTNUT TANNIN

FOMULACION Y EVALUACION DE UN PRETRATAMIENTO DE BASE ACUOSA CONTENIENDO TANINO DE CASTAÑO

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SUMMARY

In this work an aqueous primer containing chestnut tannin and phosphoric acid was developed and its anticorrosive properties assessed by different conventional tests. Treated steel panels coated with an anticorrosive paint and a topcoat were subjected to the salt spray test, humidity chamber, mechanical tests (adhesion and flexibility) and electrochemical tests (corrosion potential, ionic resistance and polarization resistance). Electrochemical tests were done employing only panels primed with the primer. 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 incorporating corrosion products to the film as ferric tannates and avoiding oxide formation. Undercutting rusting was not significant and the scratch line stood free from oxides. The good stability of the binder in low pH media and the interaction of the binder with the substrate are decisive factors in the performance of this aqueous pretreatment system.

Keywords: *corrosion protection, water-based pretreatment, acrylic emulsion, phosphoric acid, tannin.*

INTRODUCTION

Wash primers designed to protect steel structures against corrosion normally contain chromates, which, because of their toxicity, constitute a hazard that needs to be replaced by more environmentally acceptable corrosion inhibitors. In this sense tannins, a class of natural, non-toxic, biodegradable organic compound, is being proposed as an alternative in primer paint systems.

Tannins as corrosion inhibitors are applied both in solvent and in waterborne paints. Tannin based paints could be applied on partially rusted substrates, reducing in this way the effort needed for cleaning the surface by sandblasting or other methods. They have been

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referred, sometimes, as rust stabilizers modifying the active rust into an unreactive protective compound.

Solvent-based primer formulations were developed and tested employing electrochemical techniques. The total amount of iron dissolved in this case was compared with a blank consisting of steel covered either with a varnish film or with a paint system (anticorrosive paint plus a topcoat). Rusting, blistering and adhesion were also assessed over time. It was shown that paint adhesion and anticorrosive properties of the tested paints were improved when they were applied in combination with pretreatment formulations containing tannins. These pretreatments reduce steel corrosion rate by a factor of three with respect to conventional ones and may be used on clean or slightly rusted surfaces of variable roughness [1-3]. However, their behavior not only depends on their composition but also on the properties of the whole paint system. Results showed that tannins could not be employed alone when subjected to different tests [1-5].

The reaction mechanism of tannins added to priming paints for steel protection is not well understood and their efficiency questioned by some authors [4, 6-9]. Tannins are polyphenols of vegetal origin and the vicinity of hydroxyl groups on the aromatic rings makes them able to form chelates with iron. Ferric tannates of dark blue color are highly insoluble and act as electric insulators between cathodic and anodic sites on the metal surface [4, 5, 8-13]. The influence of phosphoric acid on the performance of these systems, has also been studied [14, 15].

Scarce information concerning the preparation and performance of aqueous pretreatment systems containing tannins was found in the literature [3, 16, 17] although formulations without incorporating a resin have been developed [18]. It is the aim of this research to formulate a water based anticorrosive primer and to study its anticorrosive performance through mechanical, chemical and electrochemical assays. The synthesis of the binder was carried out in the laboratory in order to achieve a product with well-defined parameters and compatible with the characteristic acidity of this type of products.

EXPERIMENTAL

Pretreatment system formulation and application

Binder. The film forming material was an all acrylic emulsion prepared in the laboratory by semicontinuous emulsion polymerization. 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 persulfate (KPS), were of analytical grade and used without further purification. Distilled water (DW) was used throughout the synthesis of binder.

Polymerizations were carried out using a two-piece reactor composed of a conical-based glass vessel (capacity 1.30 dm³, with a thermostatic jacket and sampling utility) and a five-necked cap. The cup 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 I.

Table I

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 procedure for emulsion polymerization was as follows: the initial SLS was added to the water in the reactor followed by all the EA (the less reactive monomer) and a fraction of the MMA and EGMA (Table I), with stirring. Nitrogen was passed through the emulsion during 30 minutes while heating up to 60 °C. The initiator was dissolved in 30 mL of DW, preheated and then poured into the reactor chamber. The emulsion was allowed to react for ca. 15 min, during which *in situ* seed particles were formed; then the feed was started at ca. 2 g of emulsion per minute. The flow rate of emulsion was adequately adjusted to add the MAA in the last part of reaction. An emulsification apparatus was used to prepare the monomer emulsion by stirring at 1500 rpm. The emulsion was then placed in a dropping funnel and deaerated for 30 minutes.

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 [19], and the glass transition temperature (T_g) was calculated using the Fox's equation. Surface tension was measured by means of the Du Noüy tensiometer (Table II). More experimental details on binder characterization are given in a previous paper [20].

Table II

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 (T_g)	35 °C

Tannin. Chestnut tannin was selected for being more reactive than mimosa and quebracho tannins; as demonstrated in a previous research it exhibits the highest reaction rate with steel [5].

Primer manufacture. Typical preparation is as follows: 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 treated according to a process to be patented to enhance its adhesive strength on steel [21]. The treated tannin was filtered off to eliminate insoluble matter and mixed with a 40% aqueous solution of the resin prepared as described above plus 2 mL of Texanol[®] and a flash rusting inhibitor [21]. The system was allowed to stand during 24 hours and filtered off again if necessary.

Application. The wash primer was brush applied on SAE 1010 steel panels (15.0x7.5x0.2 cm), previously degreased with toluene, up to a dry film thickness of $10 \pm 2 \mu\text{m}$. Test panels had a low surface roughness (average roughness $0.78 \mu\text{m}$ and a valley to peak distance of $4.96 \mu\text{m}$) and a slight oxidation. This low surface roughness was selected to perform the tests in a disadvantageous condition with respect to the adherence of the first coat. Surface roughness was measured employing a Hommel tester Model T1000 magnetic device. Treated panels were kept in the laboratory atmosphere (RH $65 \pm 5\%$ and $20 \pm 2^\circ\text{C}$) during 7 days. Then panels were covered with different paint systems as it can be seen in Table III. The anticorrosive paint was formulated with a medium solvent borne alkyd binder and contained zinc molybdenum phosphate; its anticorrosive performance was assessed in a previous research [22]. The topcoat was also an alkyd paint containing 20 % of resin (the same employed for the anticorrosive paint), 20 % of titanium dioxide and 60 % of solvent (white spirit). The solvent-borne coats were employed to make the painting scheme resistant to the salt fog test.

Table III

Tested paint 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 primer film thickness was $10 \pm 2 \mu\text{m}$. 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.

Laboratory tests

Accelerated tests, salt spray and humidity cabinet, were carried out to evaluate corrosion and water resistance of painted panels. Mechanical assays, such as flexibility and adhesion, were performed and it was expected that adhesion measurements could give an insight of metal-primer interaction. Finally, the anticorrosive behavior was monitored by direct current (d.c.) electrochemical measurements.

Salt spray test (ASTM B 117). A scratch line was made through the coating with a

sharp instrument so as to expose the underlying metal to the aggressive environment. After a 400 hours exposure, the panels were evaluated to establish the rusting degree (ASTM D 610) and failure at the scribe (ASTM D 1654). In all cases the experiences were carried out in triplicate, determining the mean value of the results obtained in the test. After visual examination, alkyd paints were removed by means of a hot 5 % sodium hydroxide solution ($65^{\circ}\text{C} \pm 5^{\circ}\text{C}$) to observe the film with a Nikon binocular stereoscopic magnifier.

A set of primed panels was left under laboratory conditions during two years.

Humidity cabinet test (ASTM D 2247). Panels were exposed at $38 \pm 1^{\circ}\text{C}$ during 250 hours and the degree of blistering was evaluated according to the ASTM D 714-87 standard specification. Afterwards, as it 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 3111). The 3 mm mandrel was chosen to perform this test in the more disadvantageous condition.

Adhesion (ASTM D 4541). Adhesion measurements were carried out on treated panels and on panels covered with the paint systems mentioned in Table III.

Electrochemical tests on treated steel panels. The cells to measure the corrosion potential across the paint film-steel substrate interface with respect to the calomel electrode, were constructed by delimiting 3 cm^2 circular zones on the painted surface by means of a cylindrical open acrylic tube, with one flat end. The measurements were done employing a high impedance voltmeter.

The ionic resistance between the steel substrate and a platinum electrode was also measured employing the cells previously described and an ATI Orion, model 170, conductivity meter that operates at a 1000 Hz frequency. Similar measurements were performed on uncoated steel.

The polarization resistance of the painted specimens was determined as a function of time employing a similar cell but with three electrodes. Calomel was the reference electrode and the counterelectrode was a platinum grid. The voltage scan was $\pm 20\text{ mV}$, starting from the corrosion potential and compensating the ohmic contribution. Measurements were done with an EG&G PAR Potentiostat/Galvanostat, Model 273A and the software SOFTCORR 352.

In every case, a 0.5 M sodium perchlorate solution was employed as supporting electrolyte and the time measurement was one week.

RESULTS AND DISCUSSION

Binder. The acid binder employed in this research had 47.7% of solids and average particle diameter of 144 nm. The complete set of latex parameters are presented in Table II. As stated above the binder has a good colloidal stability at low pH, due to a combined stabilization

mechanism of the sulfate from surfactant and the carboxylic groups from methacrylic acid.

Primer manufacture and application. Tannin is made more reactive towards steel by allowing it to combine with phosphoric acid through a chemical reaction yielding a product that resulted more acidic than phosphoric acid itself. The acid constant of this product was determined by potentiometric measurements according to a well-known analytical procedure [23] and it was found to be equal to 4.0×10^{-2} while the first acidic constant for phosphoric acid is 7.0×10^{-3} .

Once the primer was applied on steel, the surface turned quickly to a black color because of the formation of an association compound known as "iron tannate". The tannate, is actually formed by chelation of ferric cations coming from oxide or from steel dissolution as a consequence of the pretreatment acidity. On this black iron tannate-acrylic resin film different systems were applied (Table III) to conduct accelerated tests and the adherence one.

Salt spray test (ASTM B 117). The pretreatment film applied on steel, without topcoating cannot be tested because it was destroyed after one-day exposure. Regardless of the zones adjacent to the scratch line, the paint systems numbered 1, 3 and 4 in Table III, showed an acceptable behavior during this test, according to ASTM D 610. On the other hand the system number 2 exhibited bad anticorrosive performance due to the high porosity of the anticorrosive paint (PVC/CPVC 0.8) and failed at the end of a 250 hours exposure period (Table IV).

Table IV

Evaluation of failures in the tested panels

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

Microscopic examination after removing the alkyd paints (3.3X) revealed that the pretreatment film remained undamaged in the coated panel that corresponds to system 3 (Fig. 1). Some cracks were formed, in certain regions in its surface, probably, during the film redrying process after performing the test; however, no corrosion signs on the base metal were observed at the bottom of the cracks. The absence either of anticorrosive paint (system 1) or topcoat (system 2) led to a partial destruction of the primer and underfilm oxide growth (Fig. 2). Although panels coated with the anticorrosive paint and the topcoat primer (system 4) showed a good finishing after this test, the removal of the paint revealed the presence of red iron oxide spots on the substrate.

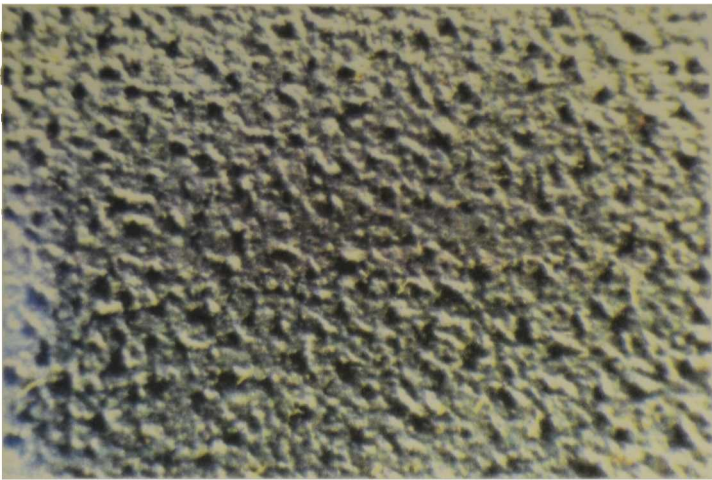


Fig. 1. Aspect of the ferric tannate film after 400 hours exposure in the salt spray test of a treated panel covered with an anticorrosive paint plus a topcoat (system 3, Table III).

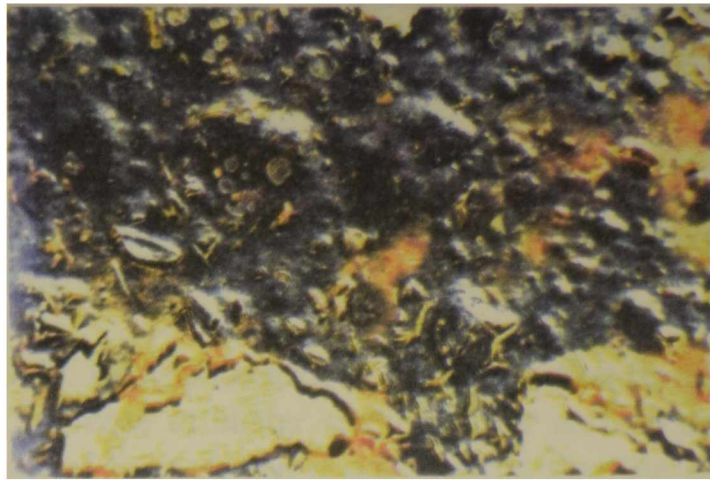


Fig. 2. - Aspect of the ferric tannate film after 400 hours exposure in the salt spray test of a treated panel covered with an anticorrosive paint without a topcoat (system 2, Table III).

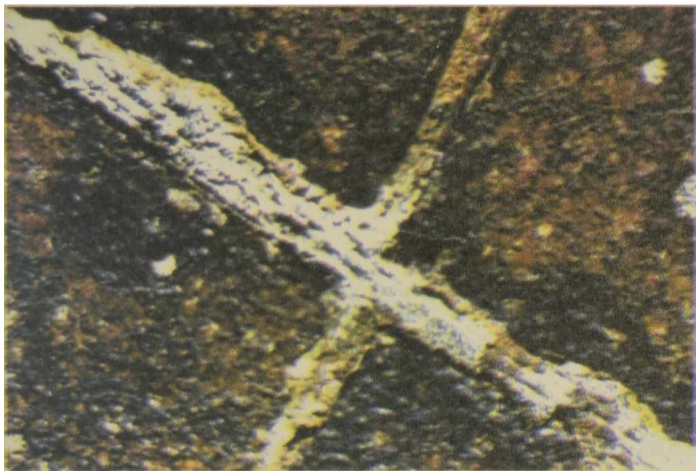


Fig. 3. – Aspect of the ferric tannate film at the scratch line after 400 hours exposure in the salt spray test of a treated panel covered with an anticorrosive paint plus a topcoat (system 3, Table III).

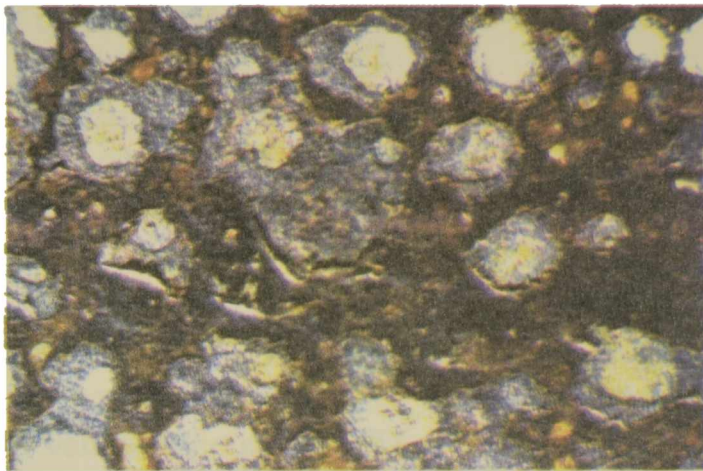


Fig. 4. - Aspect of the ferric tannate film after 250 hours exposure in the humidity chamber of a treated panel covered with an anticorrosive paint without a topcoat (system 2, Table III).

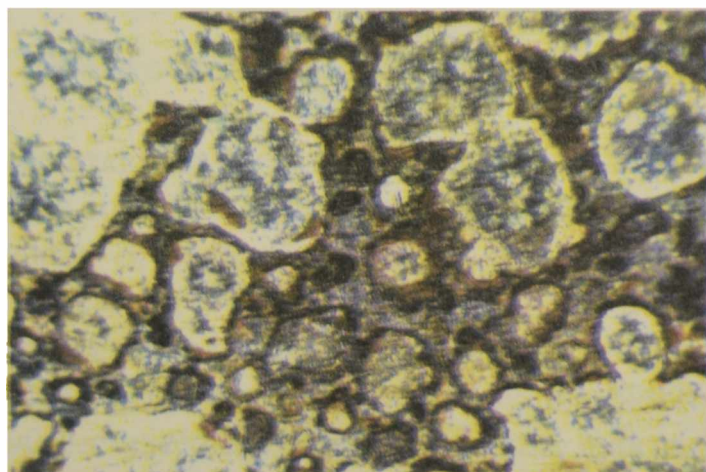


Fig. 5. - Aspect of the steel surface after 250 hours exposure in the humidity chamber of a panel covered with an anticorrosive paint plus a topcoat (system 4, Table III).

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 color turned from black to red (Fig. 3). Failure at the scribe was diminished by the presence of the tannin primer film (Table IV).

These results confirmed the well-known fact that tannin can be only employed in complete paint systems when subjected to severe exposures [4, 9].

Humidity cabinet test (ASTM D 2247). Blisters developed during the first three days of exposure. After this period no significant increase in blister size or blister surface density was observed. Blisters were broken at the end of the test and it was noticed that the loss of adherence had taken place firstly at the wash primer anticorrosive paint interface and then at the steel-wash primer film interface. No corrosion products were observed in the delaminated areas in the case of system 3. The absence of either anticorrosive paint (system 1) or topcoat (system 2) led to film destruction and oxide growth, as can be seen in Fig. 4, that corresponds to paint system 2. Pretreatment film absence also led to oxide development (Fig. 5). Table IV shows the results of different tests for the four paint systems.

Flexibility by mandrel bend test method (ASTM D 3111). The primer film containing tannin behaved satisfactorily in this test and no cracks were observed within the film after bending.

Adhesion (ASTM D 4541-89). The adhesion values obtained for panels covered with the primer alone are relatively high. 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 recorded in Table V (systems 2-4) and it was noticed that film rupture was principally of the cohesive type in the alkyd paint, remaining a thin white film from the anticorrosive coating on the black pretreatment. Adhesion was reduced after the salt fog chamber test in the intercoat zone between the primer and the alkyd system.

Electrochemical tests on treated steel panels.

Corrosion potential measurements (Fig. 6) on treated panels showed that the primer protected the substrate because the corrosion potential remained more positive (+104 mV) with respect to the corrosion potential of bare steel after 7 days of immersion. This behavior is film thickness dependent, since when it diminished from 10 to 5 μm the anticorrosive behavior was lower as it may be deduced from the shifting in the corrosion potential. Formulations without tannin are claimed to have good anticorrosive properties [24-26]; however, it could be seen that corrosion potential decreased as a function of time, approaching the value corresponding to bare steel (-750 mV vs. SCE) as well as it was observed with lower film thickness. The initial protection achieved with the free tannin primer may be attributed to phosphoric acid which by itself is not able to produce an effective phosphatizing of the steel surface. White ferrous phosphate (vivianite) and some light brown ferric phosphate may appear

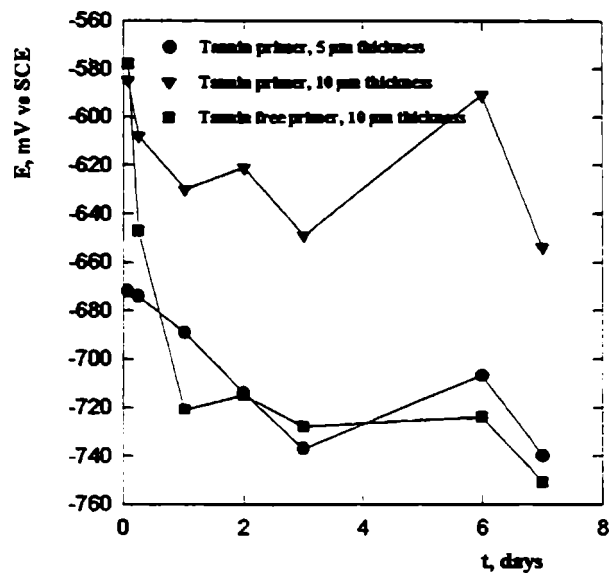


Fig. 6.- Corrosion potential of treated steel as a function of the exposure time in 0.5 M sodium perchlorate solution.

on the steel surface treated with phosphoric acid. In the presence of tannin these phosphates are readily converted into the more stable ferric tannate.

Table V

Adhesion (ASTM D 4541-89)

Systems	Adhesion (kg.cm ⁻²)	Adhesion after the salt fog chamber exposure (kg.cm ⁻²)
Pretreatment	20 ± 5	—
1	10 ± 5	5
2	9 ± 5	3
3	9 ± 5	6
4	10 ± 5	7

The measured ionic resistance (solution resistance and paint film resistance) is low and slightly higher than the solution resistance (70 Ω.cm⁻²); in this sense the pretreatment barrier effect to the electrolyte solution may be neglected (Fig. 7). The slight increase with time may be due to the sealing of pores having small and medium radii and to some oxide formation in the paint film [26, 28]. Polarization effects are negligible at the measuring frequency employed in this test.

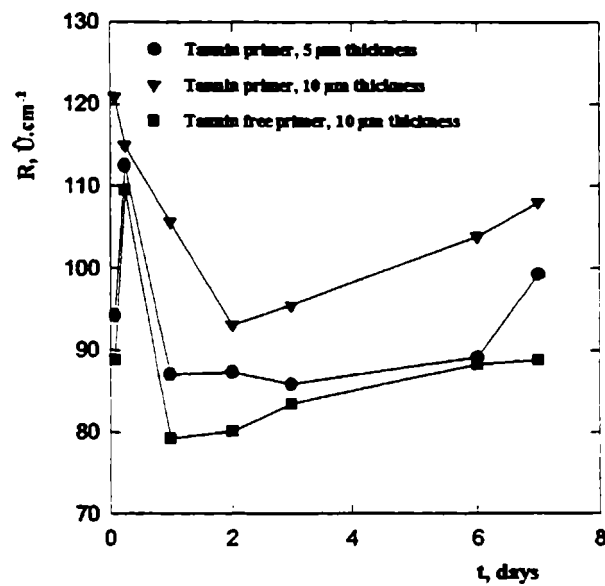


Fig. 7.- Ionic resistance of treated steel as a function of the exposure time in 0.5 M sodium perchlorate solution.

The polarization resistance (Fig. 8) of panels coated with the primer containing tannin decreased as film thickness increased. It is thought that as tannins have a great affinity for iron ions to form ferric tannate, steel corrosion increased [5] and polarization resistance diminished as tannin content increased within the film. However, polarization resistance is higher than the ionic resistance indicating that precipitated ferric tannate and the polymer of the binder blocked the active sites on the metallic surface protecting steel by a kinetic hindering mechanism [27]. In the case of the formulation tannin with lower film thickness, it is thought

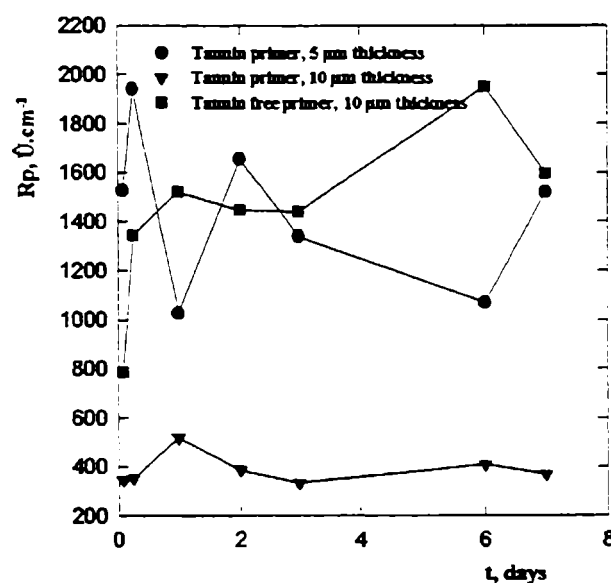


Fig. 8.- Polarization resistance of treated steel as a function of the exposure time in 0.5 M sodium perchlorate solution.

that tannate formation competed with oxide grow and the behavior approached that of the free tannin pretreatment for which polarization resistance increased as a consequence of oxide generation within the film. Fluctuations during the test are attributed to pore blocking and unblocking by corrosion products.

CONCLUSIONS

1. The pretreatment tested in this research protect adequately steel against corrosion in laboratory ambient. To achieve a good anticorrosive protection in aggressive environments an adequate paint system (anticorrosive + topcoat) must be applied.

2. The pretreatment system with tannin also gives an excellent protection against undercutting rusting.

3. The presence of tannins enhanced film adhesion to the substrate.

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

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