CHEMICAL AND ELECTROCHEMICAL ASSESSMENT OF TANNINS AND AQUEOUS PRIMERS CONTAINING TANNINS

EVALUACION QUIMICA Y ELECTROQUIMICA DE TANINOS Y DE IMPRIMACIONES ACUOSAS A BASE DE TANINOS

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SUMMARY

When the mechanical cleaning of metallic surfaces is not possible, some chemical treatments are an important possibility. The benefit of using acidified aqueous suspensions of tannins in this field has been recognized for more than thirty years. However, little is known about the action of these substances on rusted surfaces. Thus, the chemical reaction of tannins with soluble and precipitated ferric species was studied. The influence of the phosphate anion was also considered.

At the same time, cleaned and oxidized steel surfaces, treated with tannin suspensions were analyzed by microscopy and scanning electron microscopy (SEM) to observe the surface film morphology.

Four tannins were selected to carry out this investigation: quebracho, sulphitated quebracho, mimosa and chestnut.

The experimental results show that each tannin reacts with soluble and precipitated ferric species in a different way. This reaction depends on the pH of the solution. The tannate film formed on the steel surfaces had a plate morphology which also depended on the tannin. The presence of phosphoric acid contributed to the tannate film building.

Keywords: *tannins, phosphoric acid, surface conversion, ferric tannate, plate morphology.*

INTRODUCTION

The performance of an organic coating mainly depends on the metallic surface condition as well as the environment aggressiveness. The application of a good paint on a contaminated or rusted surface results in early failure of the coating. The complete removal of rust is a very important condition to enhance the coating durability.

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A metallic surface may be prepared either by chemical or mechanical methods. Recently, metallic surfaces derusting by fungii has been reported **[1]**. The sealing of metal-oxide structures with plastics cured in-situ was also proposed **[2]**.

In some cases, an exhaustive surface cleaning is impossible and chemical treatments are an important alternative. Thomas **[3]** registered more than 100 commercial products to be applied on poorly prepared steel substrates. They work by different mechanisms: oxide impregnation, stabilization, conversion and inertization. According to the author, the best results were obtained with barrier paints or with red lead pigmented primers. These paints also perform well in surfaces contaminated with chloride and/or sulphate ions.

The usefulness of anticorrosive primers and pretreatments based on aqueous suspensions of tannins acidified with phosphoric acid has been recognized during the last 30 years. In order to convert surface oxide films, tannins are employed in three different forms.

Acid aqueous suspensions of tannins may be used directly on rusted surface after wire brushing; the remaining material is generally removed by washing **[4]**. These formulations have, as a general rule, bad wettability and surfactants must be used together with low evaporation rate solvents to achieve good brushability. The phosphoric acid and tannin concentrations may reach 55 % and 10 % respectively **[5]**.

Wash primers are formulated adding a water soluble resin to fix the non-adherent products resulting from the oxide layer conversion. This would also help further painting of the metallic surface.

The penetration rate of the above mentioned formulations depends on the solvent employed, the tannin concentration and the oxide layer structure; thus, a 10 % butanol solution proved to be the best solvent and 10% is the recommended concentration level. The highest the tannin concentration the lowest the penetration rate. The optimum phosphoric acid concentration is 10 %. Free resins formulations penetrate deeper inside the oxide layer **[6, 7]**.

According to the results obtained with mimosa tannin **[8]**, these pretreatments are useful in the following conditions:

a) when the substrate preparation is poor,
b) when it is necessary to wait some days, after cleaning of the surface, to paint it,
c) when the thickness of the anticorrosive primer is reduced, and
d) when it is necessary to paint in wet ambients.

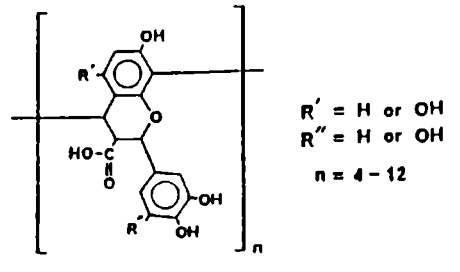
In the case of an oxide layer contaminated with chloride, sulphate, etc., the employment of rust converters combined with an anticorrosive primer is mandatory **[8-10]**.

DesLauriers **[4]** claims that the performance of these systems depends on both the amount of oxide present on the surface and the barrier properties of the complete painting scheme. This is true despite of the ability of the particular tannin to form ferric tannate. Commercial formulations, tested by other researchers, failed in all laboratory tests **[11]**.

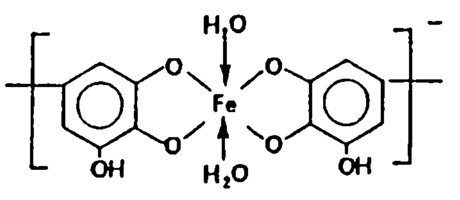
Tannins may be also employed as anticorrosive coats. Bruzzoni et al **[12]** investigated several commercial rust converters in comparison with a conventional alkyd anticorrosive paint. All formulations showed similar protective action when applied on cleaned substrates. The presence of magnetite was not detected among the oxides present on the metallic surface. As time elapsed, oxides evolved to the most harmful lepidocrosite. These paints must be used in combination with either zinc chromate or red lead primer when the converter film thickness is low (20-25 μm) **[13]**.

Anticorrosive paints with ferric tannate were proposed in the literature, for poorly prepared substrates, with promising results **[14, 15]**.

From a chemical point of view, the term tannin is applied to an extract of certain plants which contains polyhydric phenols within its structure. According to DesLauriers **[4]**, they may be represented by the next formula:



Tannins react with the oxide layer giving a black ferric tannate film, 10 μm in thickness and highly reticulated. Ferric tannate is a non crystalline substance. The film would also contain free tannin. The iron content in the film is about 2.5 % **[8]**. The structure of the complex ferric tannate may be represented as follows **[4]**:



The formation of magnetite could not be demonstrated. Joseph and Vallejos **[16]** detected the interaction between tannin and the extender pigment present in the formulation. Converted oxide layers contain ferrous cation coming from the reducing action of tannins on γ-FeOOH **[13, 17]**.

The time for tannins to react with iron oxides is 3 hours as minimum, however, 12-24 hours is waited before painting. Tannins yield 20-30 $m^2.l^{-1}$ and are compatible with red lead, zinc chromate and zinc phosphate primers. Tannins may be employed with: alkyd, chlorinated rubber, epoxy, phenolic, polyurethane and polyester resin **[9]**.

Tannins suspensions are more corrosive than distilled water. However, ferric tannate films formed on a steel substrate have some protective properties, depending on the surface chloride concentration **[19]**.

Phosphoric acid is usually incorporated to formulations containing tannins. Several researchers suggested that phosphoric acid would yield to the formation of a passive layer of ferric phosphate. Likewise, Mössbauer spectroscopy demonstrated that ferric phosphate is not formed for phosphoric acid concentrations below 8.5 M **[20]**.

Other substances than tannins able to stabilize iron oxide films has been reported **[21-24]**.

Rust converters based on a resin and phosphoric acid, without tannins, which can act on cleaned and rusted substrates have been developed. In some cases, they showed a performance similar to that of zinc chromate and red lead primers **[25-28]**.

The purpose of this paper is to study the reaction among tannins and cleaned and rusted steel. It attempts to specify some features of the iron oxides-tannins interaction for optimizing current rust converters formulations. Four tannins were chosen to carry out this research: "quebracho", sulphitated "quebracho", mimosa and chestnut. The employment of other less difussed tannins such as pine **[29]**, oak **[30]** eucaliptus saligna **[31]**, etc. have been reported, but they are not considered here.

The first stage of this investigation comprised the study of the reaction among the selected tannins and the ferric cation at 2.0, 4.0, 6.0 and 8.0 pH values. The mass of tannin precipitated for a given amount of ferric cation, in every case, the influence of the phosphate anion on the complexing capacity of tannins, at the same pH values as well as the reactivity of the four tannins with ferric hydroxide were investigated.

During the second stage, the morphology of the products formed on cleaned and rusted steel surfaces by tannins was determined employing optical microscopy and SEM.

The steel corrosion rate in tannins suspensions was also evaluated. Finally, a primer containing tannin was formulated and its anticorrosive performance evaluated through corrosion potential measurements.

EXPERIMENTAL AND RESULTS

Reactivity among tannins and ferric cation as a function of pH

A solution of each one of the four tannins employed ("quebracho" (Schinopsis sp), sulfitated "quebracho", mimosa and chestnut) was prepared as follows: 10 g of tannin was placed in a 400 ml beaker and suspended in 400 ml of hot water (90 ºC); then, 50 ml of 1 M potassium nitrate was added to coagulate colloidal substances and the system was left 24 hours in repose, filtered and transfered to a 500 ml volumetric flask.

10 ml of a 10 $g.l^{-1}$ ferric nitrate solution and 10 ml of the 1 M potassium nitrate solution were placed in a 250 ml beaker. Afterwards, 100 ml of the tannin solution was added and the pH value adjusted to 2, 4, 6 or 8. After 24 hours the pH value was controlled and adjusted to the original ones. 24 hours later, the pH was measured again and the suspensions filtered. The amount of both the tannin and the iron precipitated were determined by drying at 100 ºC and calcination at 1000 ºC, respectively.

The working temperature was 20 ± 1 ºC.

The precipitated form of tannin and ferric species is a ferric tannate whose IR spectrum coincides with the spectrum of tannin alone.

The results plotted in **Fig. 1** show that the maximum reaction capacity of tannins with soluble ferric species increased together with pH, this is the mass of tannin precipitated for a given amount of iron increased as pH did. The highest the amount of precipitated tannin the best the quality of the obtained film **[8]**.

Chestnut tannin showed higher reaction capacity at low pH values; which was exceeded by mimosa tannin as pH increases. Finally at alkaline pH values such a capacity for sulphitated tannin exceeded the corresponding to the other tannins.

From data in **Fig. 1**, at pH = 4, it may be calculated that chestnut precipitated the highest amount of tannin per mmole of ferric cation, 700 mg; while mimosa, "quebracho" and sulfitated "quebracho" 560, 500 and 195 mg, respectively. Those amounts represent the highest amount of each tannin reacting with a given amount of ferric cation in the conditions of the experiment.

As it was stated in the literature **[33]**, ferric tannates resulted insoluble compounds, which precipitated fron tannins suspensions when ferric cation was added. They are non adherent compounds and surfaces treated with acid aqueous suspensions of tannins must be washed to eliminate loose reaction products. Instead, primers are formulated with resins in order to fix the loose tannates resulting from the conversion of the steel surface **[4]**. Ferrous tannates are soluble in water, colourless and easily oxidable **[33]**.

Reactivity among tannins and ferric cation as a function of pH in the presence of phosphate anion

The procedure employed in this case was similar to the former one with the exception of 2.0 g of phosphoric acid added to the beaker containing the ferric cation. The precipitated was analyzed to determine the amount of tannin, iron and phosphate present. Phosphate content was determined by a gravimetric technique **[32]** and the results plotted in **Fig. 2**.

Phosphate anion and tannins compete for the ferric cation; therefore, the presence of that anion diminishes the amount of tannin precipitated for a given amount of iron. Chestnut tannin is the less affected by such competition because it precipitated 87.3% (at pH = 4) of the amount of tannin consigned in the preceeding paragraph; while mimosa, "quebracho" and sulfitated "quebracho" 49.5, 7.80 and 5.70% respectively. These calculations were made from data in **Fig. 2**. However, the presence of phosphoric acid is necessary because it acts on clean steel surfaces contributing to iron oxides dissolution, generating the ions to form the ferric tannate film. Likewise, it improves the wetting properties of tannins suspensions.

Reactivity among tannins and precipitated ferric hydroxide as a function of pH

10 ml of a 10 $g.l^{-1}$ ferric nitrate solution and 10 ml of the 1 M potassium nitrate solution were placed in a 250 ml beaker. The pH value was adjusted to 2.0, 4.0, 6.0 and 8.0, respectively. The system was allowed to repose for 24 hours. The same procedure was performed but employing the solution of each tannin in water. After 24 hours the content of each beaker was mixed and the pH adjusted. The pH adjustement was repeated 24 hours later and the systems allowed to repose one day more. Finally, the solids present in each beaker

were filtered and both tannin and ferric contents determined according to the procedure described in the first paragraph of this section. Results are shown in **Fig. 3.**

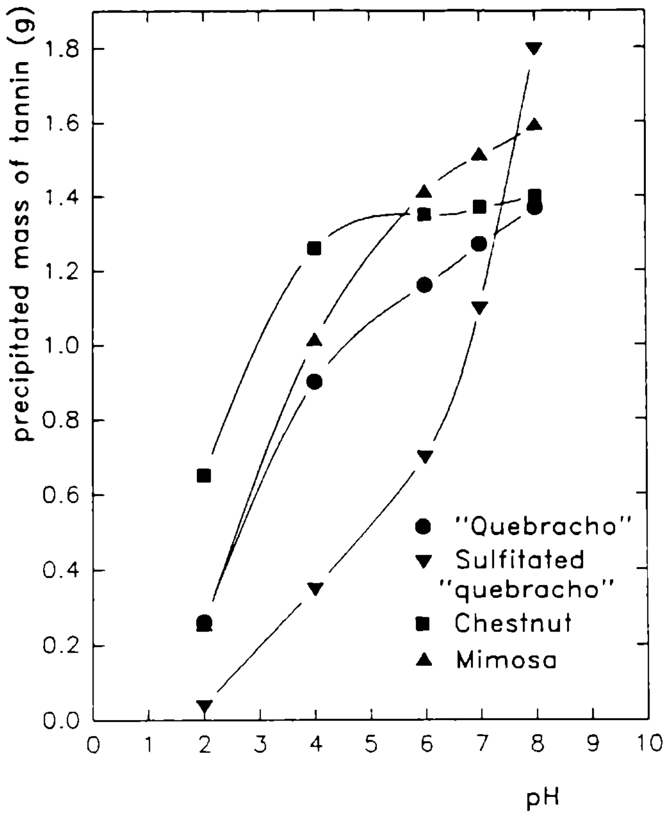


Fig. 1.- Mass of tannin precipitated from 1.79 mmoles of soluble ferric cation as a function of pH, for the different tannins.

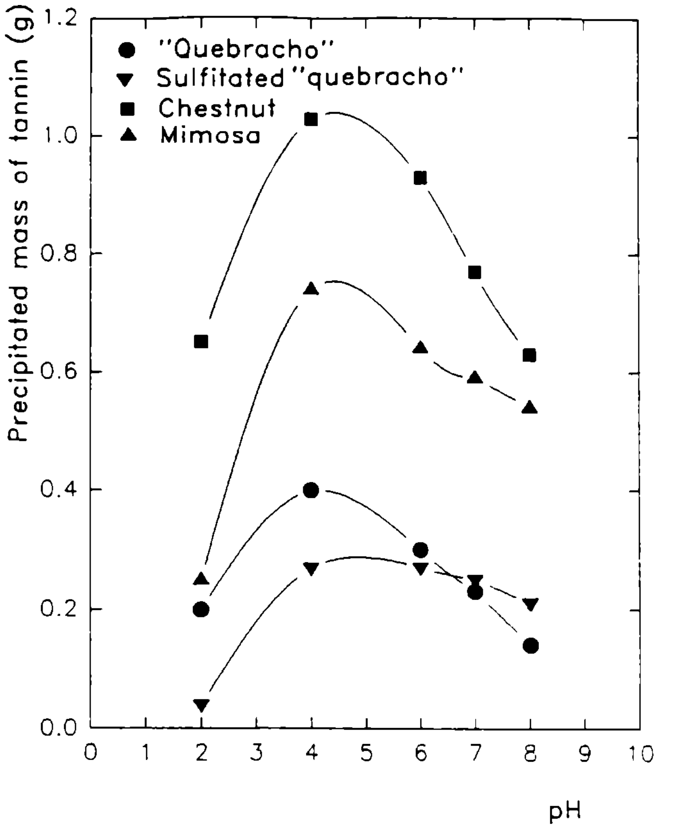


Fig. 2.- Mass of tannin precipitated from 1.79 mmoles of soluble ferric cation in the presence of 20.0 mmoles of phosphoric acid as a function of pH, for the different tannins.

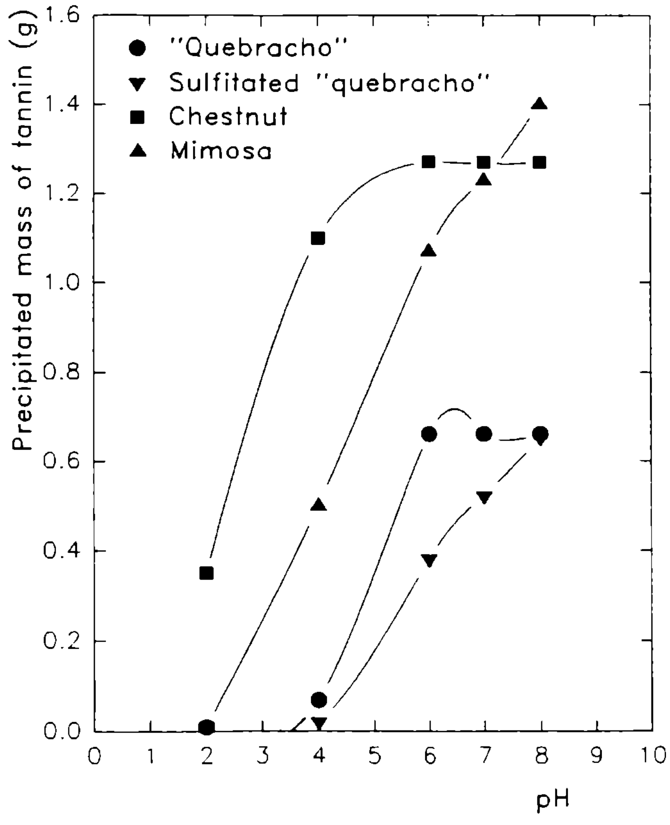


Fig. 3.- Mass of tannin precipitated from 1.79 moles of precipitated ferric hydroxide as a function of pH, for the different tannins.

Comparing **Figs. 1** and **3**, it may be seen that the reaction capacity of tannins with precipitated ferric hydroxide is less than the one observed with soluble ferric cation. It also depends on the tannin tested. Chestnut tannin is the most reactive while "quebracho" and sulphitated "quebracho" are the less reactive tannins. From data in **Fig. 3**, at pH = 4, it may be calculated that chestnut precipitated 81.8% of the precipitable tannin per mmole of ferric cation; while mimosa, "quebracho" and sulfitated "quebracho" 73.3, 44.4 and 77.1 %, respectively.

The curves in **Fig. 3** have a similar shape. The amount of tannin reacting with iron increased as pH did up to the interval 3.0-5.0; in this zone the curve presents a maximum. The initial increase is attributed to the tannin deprotonization which favours ferric cation complexation. At higher pH values the ferric hydroxide precipitation competes with the formation of ferric tanate reason by which the amount of precipitated tannin diminished. The pH interval 3.0 - 5.0 is the optimum zone to form the ferric tannate film. As tannins react with precipitated iron hydroxide in a lesser extent, unreacted tannin may combine with soluble ferric species formed lately by corrosion.

Morphology of surface compounds formed by tannins on pickled AISI 1010 steel panels

This study was carried out employing pickled AISI 1010 steel panels (C: 0.12 %, Si: 0.01 %, Mn: 0.35 %, S: 0.02 %, P: 0.02 %). Panel dimensions were 10.0 x 1.5 x 0.1 cm. They were degreased with calcium hydroxide and washed with distilled water.

The panels were treated with 5 % tannin suspensions keeping their natural pH (**Table 1**) or modifying their pH to 2.0 and 4.0 with nitric and phosphoric acid, respectively. Time reaction was 48 hours.

TABLE 1

Corrosion rate of pickled AISI 1010 panels in aqueous suspensions of tannins

Tannin	pH	Corrosion rate $mg.cm^{-2}.day^{-1}$
"Quebracho"	3.83	0.227
Sulphitated "Quebracho"	4.14	0.402
Mimosa	4.40	0.227
Chestnut	3.09	0.505
Blank	7.00	0.140

NOTE: pH values measured in a suspension containing 0.5 g of tannin in 50 ml of distilled water

Once the reaction took place, the panels were observed by means of a microscope (40X). The morphology was studied by SEM (350X in most cases). Then, loose reaction products were removed by brushing and the observations repeated. Aqueous suspensions of tannins react with ferric ions produced by steel corrosion generating a black iron tannate film.

"Quebracho" tannin showed the best spreading ability on steel surfaces while chestnut and sulphitated "quebracho" tannins the worst. The spreading ability is highly improved when phosphoric acid is added to the formulation. Corrosion of the base metal was observed in sites when the liquid film did not cover the metal surface. By this reason many commercial products incorporate surfactants in their formulation [5].

For tannin suspensions at their natural pH, a microscopic analysis (40X) showed that "quebracho" tannin formed the best film on the steel surface. It also showed good adherence to the substrate. Underfilm corrosion was observed in the case of chestnut and sulphitated "quebracho" tannins. For the sake of simplicity, photographs and micrographs of panels treated with mimosa tannin (**Fig. 4**) are included in this paper.

SEM analysis of treated surfaces revealed a plate morphology of tannate film, aspect which varied for the different tannins (**Fig. 5**, 350X). "Quebracho" tannin produced small plates and a highly reticulated surface; sulphitated "quebracho" originated a film with bigger plates and less cracks. All the films appeared to be loose-leaf films.

Some of the ferric tannante film remained strongly adhered to the steel substrate when the treated panel was brushed with a hard brush. The tannate film in contact with the metallic surface appeared to be more compact and less cracked. **Fig. 6** (3500X) shows the adherent film remaining after brushing.

The reactivity of tannins with cleaned steel surfaces ensures the adherence of the tannate film to the base metal [34].

"Quebracho" and mimosa tannins generated the best films due to their spreading properties and highest reactivity for pH values close to neutrality (**Fig. 1**).

Tannins suspensions in nitric medium (pH = 2) also form a ferric tanate film with a plate morphology (**Fig. 7**, 40X). However, in all the cases, underfilm corrosion at the base metal took place. Chestnut tannin treated panels showed the lowest degree of corrosion. By this the reason studies employing tannin suspensions acidified with nitric acid did not go on.

When phosphoric acid was used instead of nitric acid, it was observed that the tannate film seemed to be less cracked (**Fig. 8**, 350X). The presence of phosphoric acid diminished markedly the base metal corrosion. Both, nitric and phosphoric acids, favoured the tannate film formation. Acids allowed the dissolution of the base metal causing a homogeneous precipitation throughout the metal surface and, consequently a tannate layer of better quality.

Chestnut tannin produced the best films from suspensions acidified with phosphoric acid. In diminishing the natural pH of tannin suspensions, it may be seen that chestnut tannin reacts with ferric cation in a greater proportion (**Figs. 2-3**), generating a better quality film.

After brushing, it was observed the existence of a strongly adhered tannate film on the metal surface.

Morphology of the surface compounds formed on rusted AISI 1010 steel panels by tannins

Rusted panels were prepared from pickled AISI 1010 steel panels exposed in a chamber at 40 ± 1 ºC, wetting them periodically with distilled water, during 3 weeks. The oxide film obtained by this technique was 150 μm thick being FeOOH the most important product, which is normally found in atmospheric exposures [4]. The rusted panels were brushed with a wire brush to remove weak and not adhered corrosion products. The thickness of the remaining layer was 30 μm.

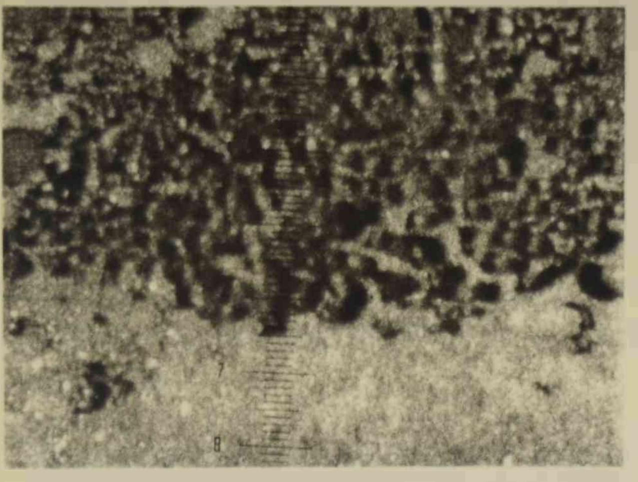


Fig. 4.- Photograph of the ferric tannate film formed on a clean AISI 1010 steel surface by mimosa tannin suspension at its natural pH (40 X).

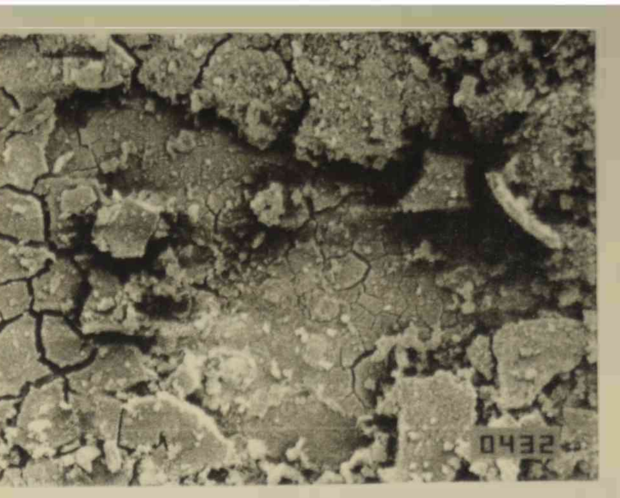


Fig. 5.- SEM micrograph of the ferric tannate film formed on a clean AISI 1010 steel surface by mimosa tannin suspension at its natural pH (350X).

Fig. 6.- SEM micrograph of the remaining of the ferric tannate film formed on a clean AISI 1010 steel surface by mimosa tannin suspension, at its natural pH, after brushing (3500X).

Fig. 7.- Photograph of the ferric tannate film formed on a clean AISI 1010 steel surface by mimosa tannin suspension at pH = 2 of nitric acid (40X).

The panels were treated with 5 % tannin suspensions keeping their natural pH value (**Table 1**) or modifying it to either 2.0 or 4.0 with phosphoric acid. Time reaction was 48 hours. Once the reaction took place, the panels were observed in the same way as pickled ones did.

When rusted steel panels were treated with tannins suspensions at their natural pH, the oxide morphology (**Fig. 9**, 350X) is replaced by a plate morphology (**Fig. 10**, 350X). The oxide present on the surface supported the tannate film leading to a less cracked film. A significant amount of non-converted rust was encountered under the tannate film formed by sulphitated "quebracho" or chestnut tannins. However, these react strongly with outer oxides. Mimosa and "quebracho" tannins produced films of higher quality; this could be attributed to their better spreading properties. Besides, the mimosa variety is highly reactive with ferric hydroxide (**Fig. 3**). Again, the presence of phosphoric acid improved film quality and reduced the base metal corrosion (**Fig. 11**, 350X).

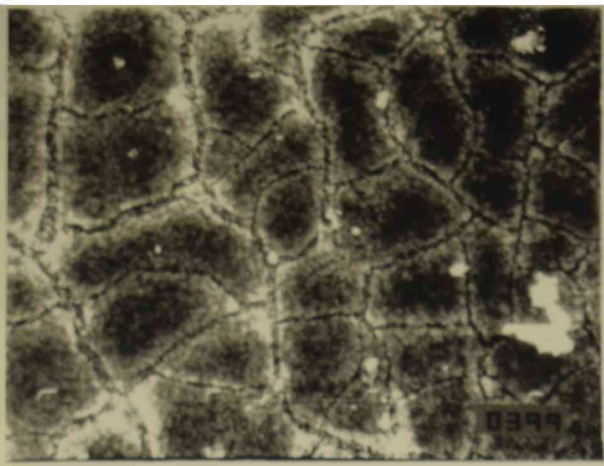


Fig. 8.- SEM micrograph of the ferric tannate film formed on a clean AISI 1010 steel surface by mimosa tannin suspension at pH = 2 of phosphoric acid (350 X).

Fig. 9.- SEM micrograph of the untreated ferric oxide morphology (350X).

Fig. 10.- SEM micrograph of the ferric tannate film formed on a rusted AISI 1010 steel surface by mimosa tannin suspension at its natural pH (350X).

Fig. 11.- SEM micrograph of the ferric tannate film formed on a rusted AISI 1010 steel surface by mimosa tannin suspension at pH = 2 of phosphoric acid (350X).

For phosphoric acid suspensions, chestnut gave very good films while "quebracho" and Mimosa tannins produced films of fair quality. This behaviour could be explained, partially, considering the curves in **Fig. 3**.

Adherence to the steel substrate and replacement of the iron oxides morphology by a plate one, indicate that tannins: a) actually convert the steel surface, b) stabilize the rusted steel surface and c) may be employed as pre-treatments on rusted steel surfaces.

Determination of AISI 1010 steel corrosion rate in tannins suspensions

This step was performed in order to know if the steel corrosion was avoided by the tested tannins. For corrosion rate determinations, 10.0 x 1.5 x 0.1 cm steel panels were placed in a 2 g tannins suspensions for 5 days, stirring them periodically. After 5 days, the panels were taken off and the total amount of dissolved iron determined colorimetrically. No adherent films formed on the steel surface kept in contact with tannin suspensions. Tannate films adhere on such a surface only when solvents are completely evaporated; these films have some corrosion resistance **[19, 35]**. Results displayed in **Table 1**, show that tannins suspensions are more corrosive than distilled water (blank), as it was stated in the literature **[18]**. The corrosion rate also varied for the different tannins; thus chestnut suspensions are the most corrosive, probably due to the more acidic properties of this tannin.

Finally, an aqueous primer containing tannin was formulated and its anticorrosive performance evaluated through open circuit potencial measurements. The composition of the primer was as follows: acrylic resin 20% by v/v, tannin 6% w/v phosphoric acid 3% w/v and corrosion inhibitor 0.3% w/v. The inhibitor to stiffle flash rusting was selected among: butyraldehyde, benzaldehyde, cyclohexanone, as it is suggested in the literature **[36]**. The primer was applied by brushing on a slightly rusted steel panel up to a thickness of 10 μm and allowed to cure for 7 days. The measurements were carried out following a procedure previously described **[37]**. The variation of the open circuit potential as a function of time is presented in **Fig. 12** toghether with the curves of the primer without tanning and the naked steel electrode.

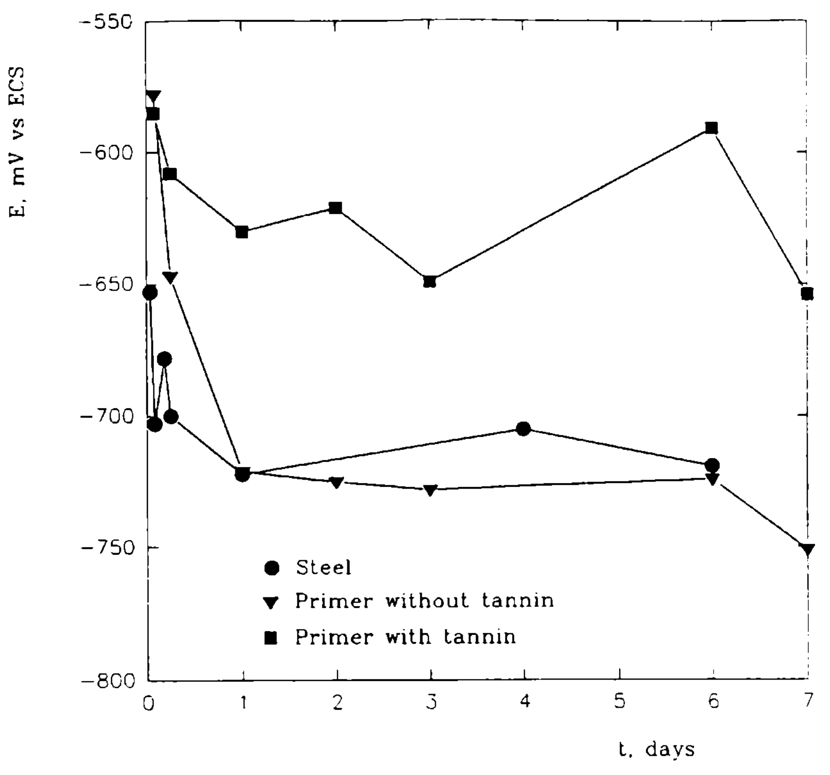


Fig. 12.- Corrosion potential variation as a function of time for steel coated with an aqueous primer containing tannin. Electrolyte: sodium perchlorate 0.5 M.

It may be seen that the primer containing tannin protected steel from corrosion because the electrode potential was shifted to the more noble values during a week. In the other cases, the electrode potential derived quickly to the steel corrosion potential. This protection was due to the presence of tannin, the sole addition of phosphoric acid was not enough to stop corrosion.

CONCLUSIONS

1. The analytical procedure previously outlined is recommended to evaluate the interaction of tannins with iron species. Previous to formulation, each tannin must be evaluated by a similar procedure to assess its usefulness in formulating anticorrosive primers.

2. The determination of pH and corrosivity of tannin suspensions may help in understanding its interaction with steel. The more acidic and the more corrosive the suspension, the greatest the interaction with steel will result.

3. The optimum pH for the tannate film to develop is comprised in the range 3.0-5.0. The values are close to the natural tannins suspensions pH.

4. The presence of phosphoric acid in the formulations passivates steel surfaces and favours the tannate film formation on cleaned steel surfaces. It also assists oxides dissolution and further reaction with tannins.

5. Tannins react with cleaned and rusted steel surfaces generating a layer with a plate morphology replacing the globular one of iron oxides.

6. Aqueous primers containing tannins do inhibit steel corrosion as it was revealed by potential corrosion measurements.

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