MANUFACTURE AND TESTING OF WATER-BASED TANNIC PRETREATMENTS

ELABORACION Y ENSAYO DE IMPRIMACIONES TANICAS DE BASE ACUOSA

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SUMMARY

The anticorrosive efficiency of the different coating systems depends to a great extent on the initial state of the metallic surface, since the best paints do not insure a lengthy protection when they are applied over a structure that is not adequately prepared. In consequence, at present the treatment of the corroded surfaces continues being a great challenge in spite of the modern existing methods, specially when the conditions do very expensive the total removal of oxides or is not practicable by diverse motives.

In a previous work, the purification and the characterisation of tannins extracted from the heartwood of quebracho (Schinopsis sp.) were performed particularly with the objective of knowing some inherent properties of the reaction between the tannins and the iron oxides. In the present work, several water-based tannic pretreatments acidified with orthophosphoric acid were formulated and manufactured at laboratory scale; results of tests carried out allowed to conclude that the application of the quoted tannic solutions on a substratum with a mechanical preparation insufficient to eliminate the totality of the products of corrosion, increased the useful life of the applied coating system, delaying oxidation and in consequence the deterioration of the subsequent paint films.

Keywords: *rusted steel, pretreatment, tannins, coating system, practical adhesion, degree of rusting.*

INTRODUCTION

In the last years important developments in corrosion-inhibiting coatings were achieved, but the anticorrosive efficiency also depends significantly on the surface preparation, since the very good paints inclusive do not insure a lengthy protection if they are applied over a surface that is not totally free of iron oxides **[1,2]**.

The treatment of the corroded surfaces continues being a great challenge, in spite of the existing methods. In the case of a totally rusty metal, the cleanliness by sandblasting or

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gritblasting generates a surface of excellent characteristics to apply the coating system; but in some cases, the blastcleaning can not be selected by the high cost, by operative problems of the structure to protect, by the difficulties in achieving an adequate coordination of the surface preparation/application of the first layer of the coating system or for ecological problems. Other mechanical treatments (brush and sandpaper cleaning, etc.) do not result efficient to eliminate completely corrosion products, particularly in pits generated by the metal dissolution as a consequence of the anodic reaction **[3-6]**.

Pretreatments based on different mineral acids present also serious limitations; salts formed in the metal/surface usually generates abundant osmotic blistering. Regarding solutions of orthophosphoric acid, they do not give a true passivity since the reaction with different layers of iron oxides is markedly heterogeneous **[7]**.

Researches carried out in many institutes of different countries employing natural products of high molecular weight to form stable complexes with the iron oxides purport to obtain an homogeneous reaction with the products of the metallic corrosion **[8-10]**. Particularly and owing to the commercial significance, tannins extracted from the quebracho wood have been object of numerous studies; these natural tannins react rapidly with the soluble iron salts forming intense blue black precipitates; the hexahydrated iron (III) ions and the hydroxy phenolic groups present in the condensed tannins gives insoluble chelates and liberates $[H_3O]^+$ which explains the major yield of the reaction as the pH increases. It is not convenient to exceed the pH 6 due to meaningful loss of tannins by oxidation **[11-16]**. Regarding the iron (II) salts in solution, although they do not form insoluble compounds with the hydroxy phenolic groups of condensed tannins; the $[Fe\ (H_2O)_6]^{2+}$ ions are rapidly oxidised to $[Fe\ (H_2O)_6]^{3+}$, specially if the reaction is carried under conditions where there is an access of oxygen to permit the oxidation and to values of reduced pH. In consequence iron (II) salts solutions instead of iron (III) ones also show the formation of blue black precipitates.

In this work diverse formulation variables of aqueous pretreatments based on tannins extracted from heartwood of quebracho (Schinopsis sp.) were studied. These water-based tannins solutions were applied over steel plates with a mechanical preparation insufficient to eliminate completely the corrosion products with the objective of establishing the influence of that variable on the anticorrosive capacity of a coating system.

EXPERIMENTAL PART

1. Extraction and purification of the tannic liquor

The sample of quebracho (Province of Chaco, Argentina) was extracted from a live and healthy tree, selecting only heartwood **[17]**. The sample was cutted, dried in stove at 50 °C until 4-6 % humidity and finally crushed in a hammer mill, choosing the fraction that passes by the 30 mesh sieve.

The extraction was carried out in a vessel with a double jacket to permit the heating (70-75 °C), employing a 3/1 distilled water/heartwood ratio in weight and stirring intensely for 1 hour. The first extraction was performed in the quoted conditions while the two subsequent washes were fulfilled in similar way but employing only the 50 % of water due to a half remains retained in the sawdust and the other one forms the liquor.

Afterwards the tannic liquor was purified to eliminate the gumresins and the insoluble components, which remain in the liquid in the colloidal state due to their small particle size. The original extract was cooled at 0-2 °C for 24 hours and then centrifuged, collecting the free-turbidity superior layer; the solids were finally washed several times with distilled water to recuperate the tannins retained.

Later, the concentration of the liquor was carried out employing a vacuum system (approximately 550-660 mm Hg at 40 °C) to avoid the serious inconveniences that generate the elevated temperatures (oxidation and loss of tannins). The final concentration was 18-20 °Be (410-450 g solid extract/1000 ml liquor) with a pH remaining between 4.5 and 5.0 according to the experiment.

An analytic solution of the purified liquor (0.4 % solids w/w) evidenced, previous acidification with drops of acetic acid, an abundant precipitate formation with the incorporation of bromine water, which indicated the presence of catechol tannins (structure strongly polymerised, with bencenic ring bonded by carbon chain); on the other hand, with the addition of a lead acetate solution to the acidified liquor, the precipitation was not significant which demonstrated that the content of pyrogall tannins (structure weakly polymerised, polyester type) is not quantitatively important in the extracts of the quebracho heartwood [11].

The method of Lowenthal allowed to determine quantitatively the content of tannins in the purified liquor [9]; it is based on fact that the tannins are oxidised in solution by the potassium permanganate in presence of indigo carmine, which is employed as indicator of the final point. The results point out the presence of 17.5 g of tannins, over 100 g of wood with a humidity of 6.3 % (one extraction and two subsequent washes in the quoted conditions) or else approximately the 91.0 % in weight of tannins over the dry extract free of insoluble components.

2. Water-based tannic pretreatments

The pretreatments were prepared in aqueous solution with different concentrations of tannins, which ranged from 2.5 to 20.0 % in weight. The pH of the solutions was regulated with an orthophosphoric acid solution until reaching values between 1.5 and 4.5 with variations of 0.5 each time. Furthermore, a wetting agent at 0.2 % level in weight was employed; 56 samples in duplicate were elaborated (8 concentrations of tannins x 7 levels of pH).

3. Test panels

a) Surface preparation

SAE 1010 steelplates were chemically pickled and sandblasted to Sa 2 ½ degree (SIS 05 59 00/67 Standard, 32 µm maximum roughness) and then exposed to natural weathering in the CIDEPINT experimental station (Table I), until reaching the total oxidation of the surface [5]. Later the corrosion products not adhered to the metallic base were eliminated by rubbing with sandpaper, observing a similar degree to C St 2 of quoted standard; afterwards the panels were washed with toluene in vapour phase.

Table I

CIDEPINT experimental station, La Plata (Argentina)

Geographic position	Latitude Longitude	34° 50' S 57° 53' W
Atmospheric conditions, 1994/1995	Mean temperature, °C Mean relative humidity, % Amount of rain, mm.year^{-1} Mean sulphur dioxide, mg.m^{-2}.day^{-1}	16.7 78.8 1104 6.6
Corrosion rate, 1994/1995	Steel, mg.dm^{-2}.day^{-1}	5.44

b) Application of the tannic solution and the protective system

A coat of tannic pretreatments was brush applied in each case. The time of reaction (4 and 8 hours) was considered as operative variable, which elapsed in laboratory ambient (relative humidity, 62-65 %; temperature, 15-18 °C).

The coating system, also applied by brush, was constituted by one film of the corrosion-inhibitive coating (40 ± 5 μm dry film thickness), one of the intermediate coating or sealer (25 ± 5 μm) and finally two top coats (40 ± 5 μm). The coating composition is shown in Table II, carrying out the preparation in a ball mill with porcelain jars of 1.0 litre total capacity.

Moreover, two test panels were prepared to be used as reference by applying directly the coating system on the weathered-sanded metallic base, without tannic pretreatment. Other two test panels included as pretreatment a single coat of a 15 % orthophosphoric acid solution.

c) Experimental trials

The whole of the prepared panels were placed in a frame and then subjected to natural weathering for 24 months. The specimens were exposed at 45 ° facing to the north. On the aged panels, the following laboratory trials were performed:

Table II

Composition of coatings, % in weight on solids*

Component	Anticorrosive coat	Sealer	Top coat
Titanium dioxide	-	-	38.2
Zinc hydroxy phosphite	33.7	-	-
Micaceous iron oxide	-	41.9	-
Red iron oxide	16.7	-	-
Micronised barytes	-	6.1	-
Micronised talc	16.8	3.1	-
Chlorinated rubber grade 20	23.0	34.2	15.3
Medium oil alkyd resin **	-	-	45.9
42 % chlorinated paraffin	9.8	14.7	-
Driers	-	-	0.6
PVC, %	45.0	25.0	15.0

* Solvent mixture: Aromasol H/white spirit, 4/1 ratio in weight
** From soya bean oil (70 % solids)

d) Degree of rusting

A visual and microscopic judgement was carried out by employing the ASTM D 610 Standard, whose scale ranges from 0 (approximately 100 % of the surface rusted) to 10 (no rusting or less than 0.01 % of the surface rusted). The intermediate values are: 9, less than 0.03 % of surface rusted; 8, less than 0.1 % ; 7, less than 0.3 %; 6, less than 1 %; 5, approximately 3 % ; 4, approximately 10 % ; 3, approximately 1 / 6 of the surface rusted; 2, approximately 1 / 3 and finally 1, approximately 1 / 2 of surface rusted.

e) Practical adhesion

The evaluation of the film adhesion was carried out by employing an Elcometer Tester Model 106, according to ASTM D 4541 Standard. The instrument is direct reading and does not include the frictional forces of the nut and bearing assembly. It has a base support ring to avoid bending of thin substrata and a cutter to remove the excess of adhesive (twin-pack epoxy resin) from around the base of the dolly.

The dolly is bonded to the coating under test; when adhesive has cured, the adhesion Tester is placed over the dolly and the claw engaged. The dragging indicator is set to zero.

Bonded dolly is subjected to progressively increasing stress at a constant rate until it fractures: dragging indicator retains the maximum pull of force reached. About 10 determinations on every test panel were performed and then the mean values were calculated.

RESULTS AND DISCUSSION

Experimental values of rusting degree as well as of the practical adhesion obtained from test panels exposed to natural weathering for 24 months are presented, respectively, in Tables III and IV. These results were statistically treated according to factorial design of the 2 x 7 x 8 type, that is 112 different combinations; each combination was prepared and tested in duplicate (replicas).

The values shown in Tables III and IV were used to calculate the sum of squares and the degrees of freedom of each effect; by dividing each sum of squares by the corresponding degrees of freedom, the estimated variance was calculated. Hypothesis zero implying that all the main effects are equal to zero, is accepted. Thus all the variance estimations would be independent and would refer to the same estimated amount by means of the residual variance, that is the magnitude of the experimental error. If the variance of the cited sources is bigger than that based on the residual error (experimental), the F test indicates that it is little probable that the observed variances ratio occurred randomly. If the F test gives a positive result, the hypothesis zero fails. In such case, it will be evident that the variance does not simply arise from the experimental error, but also from an additional variance introduced by the fact that the design modification was meaningful.

The F test indicates that the influence of the main effects studied is significant. To interpret the experimental results, the sum of the main effects were considered, Table V. As a consequence, it is concluded that to reach the **best anticorrosive protection** it is necessary to take into account the concentration of orthophosphoric acid which leads to a value of pH 1.5, the level of 20.0 % in weight of tannins and finally regarding time of reaction, to let to elapse 8 hours in ambience of laboratory before application of the first layer of the coating system.

The results also indicate that the **incorporation of orthophosphoric acid** to the tannic solutions drove to pretreatments which showed an increased corrosion resistance and furthermore an improved film adhesion, which is in agreement with the conclusions attained in the statistical study. It is convenient to mention that the tests demonstrated that to reach a satisfactory stabilisation of the metallic oxides was more effective the employment like pretreatment of some tannic solution acidified with orthophosphoric acid instead of a 15 % orthophosphoric acid solution.

After application of the pretreatment, the phosphoric acid firstly reacts with the iron oxides, furthermore, in presence of oxygen and to a strongly acid pH, the iron (II) ions are oxidised rapidly to iron (III) ions. As the pH of the solution increases by the neutralisation reactions on the metal surface, the formation of a blue black insoluble layer of iron (III) tannates is favoured. This reticulated layer would delay the oxidation reactions on the metal and in consequence the deterioration of the protective system.

Table III

Degree of rusting (ASTM D 610)
24 months of natural weathering (La Plata Station)

1. Tannic primers (4 hours) and coating system

pH of tannic solution	Level of tannins, % in weight							
	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0
1.5	4	5	5	5	6	6	7	7
2.0	4	5	6	6	6	6	6	7
2.5	4	4	5	5	5	5	5	6
3.0	4	4	4	4	5	5	5	6
3.5	4	4	4	5	5	4	5	6
4.0	3	4	4	5	4	4	5	5
4.5	3	4	4	4	4	4	5	5

2. Tannic primers (8 hours) and coating system

pH of tannic Solution	Level of tannins, % in weight							
	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0
1.5	6	6	6	7	8	9	9	10
2.0	5	5	6	6	8	9	9	9
2.5	5	5	5	6	8	9	9	9
3.0	4	5	5	6	8	8	8	8
3.5	4	5	5	5	7	7	7	8
4.0	4	5	5	5	7	7	7	7
4.5	4	5	5	5	6	7	7	7

3. Coating system (15% orthophosphoric acid solution like pretreatment)
Degree of rusting = 5

4. Coating system (test of reference, without any pretreatment)
Degree of rusting = 4

Table IV

Practical adhesion, kg.cm^{-2}
24 months of natural weathering (La Plata Station)

1. Tannic primers (4 hours) and coating system

pH of tannic Solution	Level of tannins, % in weight							
	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0
1.5	6	7	7	7	8	9	10	10
2.0	6	7	7	7	8	8	9	10
2.5	6	6	7	7	7	7	9	9
3.0	5	5	6	7	7	7	9	9
3.5	5	5	6	7	7	6	8	9
4.0	5	5	5	6	6	6	8	9
4.5	4	5	5	6	6	6	7	8

2. Tannic primers (8 hours) and coating system

pH of tannic solution	Level of tannins, % in weight							
	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0
1.5	7	8	8	9	10	11	12	13
2.0	7	8	8	9	9	11	11	12
2.5	7	7	7	8	9	10	11	11
3.0	6	6	7	9	8	9	10	11
3.5	6	6	7	8	8	9	9	11
4.0	5	6	6	7	8	9	9	10
4.5	5	6	6	7	8	9	9	10

3. Coating system (15% orthophosphoric acid solution like pretreatment)

Practical adhesion* = 7 kg . cm^{-2} (24 month weathering)
Practical adhesion* = 11 kg . cm^{-2} (72 month drying)
* Type of failure: almost completely adhesive (90 %)

4. Coating system (test of reference, without any pretreatment)

Practical adhesion* = 6 kg . cm^{-2} (24 month weathering)
Practical adhesion* = 10 kg . cm^{-2} (72 month drying)
* Type of failure: completely adhesive (100 %)

Table V

Statistical results

Main effect		Sum of the main effects	
Type	Level	Degree of rusting	Practical adhesion
Tannins, %	2.5	58	80
	5.0	66	87
	7.5	69	92
	10.0	74	104
	12.5	87	109
	15.0	90	117
	17.5	94	131
	20.0	100	142
PH	1.5	106	142
	2.0	103	137
	2.5	95	128
	3.0	89	121
	3.5	85	117
	4.0	81	110
	4.5	79	107
Time of Reaction, hours	4	271	389
	8	367	473

Regarding the **concentration of tannins** in the water-based pretreatments formulated, this variable showed a great influence on the protective efficiency. Microscopic observations permitted to determine that a great quantity of iron oxides remained on the surface after finishing the cleanliness carried out with sandpaper, previous to the pretreatment application. The surface showed pits and many iron oxides were in the interior. The tannic solutions wetted those oxides and so a great quantity of iron tannates was observed in the places where the thickness of the layer of iron oxides was major. The solutions with high content of tannins presented a more homogeneous action on the surface, which would explain the best performance reached with 20 % tannins in solution acidified at pH 1.5: the blue black chelates obtained at room temperature showed an iron content, according to atomic absorption determinations, between 2.0 and 2.5 % in weight, which would explain the before mentioned.

In consequence, the initial condition of the metallic base (roughness of the surface and mainly the remaining quantity iron oxides previous to the application of the tannic solution) would be an important variable to be considered to define the optimum level of tannins in the pretreatment composition.

Concerning the **time of reaction**, the panels with a single coat of pretreatment showed the formation of the mentioned reticulated insoluble layers just after some hours. It was evident that the tannins had not reacted completely with the corroded surface after 4 hours in laboratory ambient since brown tannic solution without reacting existed in some areas more than the blue black iron tannates. After 8 hours in the cited conditions, the reaction was completed and areas of tannins without reacting were not observed.

However, tests carried out parallely to those included in this work indicated that the optimum reaction time depends on the relative humidity of the environment in that the panels are placed after application of the tannic solution. The specimens maintained at low relative humidity (15-18 °C) showed a low rate of dark chelate formation, while at high relative humidity (i.e. 80 %) complete changes were observed.

FINAL CONSIDERATIONS

1. The visual and microscopic observation permitted to conclude that the yellow/red colour corresponding to the layer of hydrated iron oxides, after application of a tannic pretreatment, evolved toward the blue black one, making it more intense as the time was elapsing. The pretreatments with very good corrosion inhibiting behaviour (minor degree of oxidation and major value of practical adhesion) registered the cited change of color in all the thickness of the layer of iron oxides, according to observations carried out in cross sections on pretreated panels.

2. The practical adhesion performed on aged panels showed that the employment of some no polluting water-based pretreatment formulated in addition to modify the absolute fracture values, influenced on the type of failure. In spite of the high scatter of values observed, some tannic pretreatments presented an almost completely adhesive failure (break between the paint film and the substratum), but as the anticorrosive efficiency increased the coating system failed in the adhesive/cohesive form, reaching a totally cohesive fracture (cracking of the film) with the best formulated pretreatment.

3. Reference panels, without any pretreatment, showed a similar behaviour to those in which no efficient acidified tannins solutions were applied. As a consequence, the low degree of rusting and the high practical adhesion registered with some of the tannic pretreatments formulated indicate that the molecules of the purified condensed tannins extracted from the heartwood of quebracho develop complex chelates with the iron oxides on the metallic surface in the form of reticulated insoluble layers which would improve the useful life of the subsequent coating system.

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