

TIN TANNATES AND IRON TANNATES IN CORROSION-INHIBITING COATINGS

TANATOS DE ESTAÑO Y TANATOS DE HIERRO EMPLEADOS COMO PIGMENTOS INHIBIDORES EN PINTURAS ANTICORROSIVAS

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SUMMARY

The efficiency of the coating systems in the protection of metallic substrata depends fundamentally, in relation with formulation variables, on the type and content of corrosion-inhibitive pigment, the characteristics of the film forming material and the pigment / binder ratio in volume.

Concerning the pigment, there is not doubt that the use of some inhibitors in anticorrosive paints is actually an important source generating toxicity problems both for the worker and for the environment. This problem is extended to the applicator and also to the removal operation of old coatings.

*In this research tin tannates and iron tannates were employed as inhibitive pigments in anticorrosive paints. The mentioned metallic tannates were prepared on laboratory scale under controlled operative conditions, carrying out the reaction between the metallic ions and the polyphenolic groups of condensed tannins extracted from "quebracho" heartwood (*Schinopsis* sp.)*

Keywords: *corrosion, paint, pigment, inhibitor, iron tannates, tin tannates*

INTRODUCTION

The general term corrosion is commonly defined as the alteration of a material promoted by the environment. In considering the nature of the medium, metallic corrosion includes a chemical attack or an electrochemical one; environments that produce electrochemical process are characterised by their ionic conduction. As a consequence, iron and steel oxidation reaction is usually of an electrochemical type and very complex; it occurs not only on naked metallic substrata, but on those surfaces apparently covered by coatings. In the last years, the environmental pollution has led to enhance corrosion processes.

The function of an organic or inorganic film is to retard the phenomenon. From a physicochemical point of view, a coating is a system formed by dispersion of a solid or a mixture of solids (pigments) in a liquid medium called vehicle. Proper selection of the different

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components for each formulation allows the required properties of a coating or coatings to be achieved. Anticorrosive paints usually contain compounds as pigments which are particularly hazardous and besides contribute to the mentioned pollution [1,2].

Owing to the toxicity of conventional pigments and also to legal restrictions in force, many studies are carried out about non-toxic inhibitors [3-11]. Phosphates, ferrites, borates, molybdates and also silicates have been proposed; barrier pigments with lamellar structure as micaceous iron oxides were found to be effective for decreasing the corrosion rate of painted surfaces.

The aim of this paper was to carry out at laboratory conditions the elaboration of tin tannates and iron tannates to be used as non-toxic inhibitors, the assessment of their most important characteristics and finally the evaluation of the protective efficiency of formulated anticorrosive paints.

EXPERIMENTAL PART

1. Iron tannates and tin tannates preparation

1.1. Flavatannins extraction. The heartwood of “quebracho colorado” (*Schinopsis* sp., Province of Chaco, Argentina) was selected for carrying out the experiment; the sample was extracted from a live and healthy tree. The lixiviation of condensed tannins was performed according to the conditions mentioned in previous papers [12,13]. The method consisted of the crushing of the wood in a hammer mill previous drying in stove to 50 °C (4-6 % humidity), the maceration of the sawdust for 3 hours at room temperature and then for 1 hour at 70-75 °C under strong stirring (3/1 distilled water/sawdust ratio in weight), and finally the achievement of two subsequent washes to improve significantly the efficiency of the extraction.

The extracts presented marked turbidity, with a concentration of approximately 3 °Bé (60 g solid extract/1000 ml liquor) and a pH 5.2 . The composition of the extracts, expressed on dry solids, was 72-74% of tannins (method of Lowenthal), 7-8 % of no tannins (difference between the contents of the soluble components and the level of tannins) and finally 18-19 % of insoluble substances (without considering the fibres of the wood).

The extracts were purified to eliminate the gumresins and the water insoluble components, which remained in the liquid in colloidal form due to their small particle size; they were separated by centrifuging previous cooled at 0-2 °C for 24 hours. Finally, the extracts were concentrated by means of a system operating to vacuum (approximately 550-600 mm Hg), at a temperature inferior to 40 °C, reaching a final value of 18-20 °Bé (410-450 g / 100 ml liquor). These extracts showed a clear aspect, that is turbidity free, with a remaining pH between 4.5 and 5.0.

These final extracts were qualitatively characterised employing an analytic solution of 0.4 % tannins, previously acidified with drops of an acetic acid solution: abundant precipitation was observed with bromine water which indicated the presence of condensed tannins and

practically absence of precipitation with a lead acetate solution which permits to conclude that the concentration of pyrogall tannins is not meaningful from a quantitative viewpoint in the heartwood of “quebracho” employed in the experiment.

1.2. Inhibiting pigment preparation. The manufacture was carried out starting from concentrated extracts and heptahydrated iron sulphate or else dihydrated tin chloride at room temperature and under controlled conditions. The reaction between the cations and the hydroxy phenolic groups of the condensed tannins in both cases was immediate, generating a blue-black precipitate with the iron and a light brown one with the tin; the before mentioned precipitates were called iron tannates and tin tannates, respectively.

Metallic tannates were separated by centrifuging, washing with distilled water and finally drying at 50 °C until constant weight. Several trials were performed to determine the characteristics of the metallic tannates.

2. Paints formulation

2.1. Pigmentation. Experimental samples included either as inhibitor iron tannates or tin tannates manufactured according to the before described method. The zinc tetroxychromate was taken as reference pigment owing to the efficient behaviour showed up to now ; the current tendency is to proceed to its replacement due to carcinogenic action that it would present on the human being.

In all the cases, other two pigments were used together: red iron oxide and micronised talc, 50 / 50 ratio in volume. The inhibitor/inert pigment ratios were 30/70, 40/60 and 50/50 in volume.

2.2. Film forming material. The corrosion-inhibitive capacity of a paint depends, among several variables, on the active pigment as well as on the film forming material.

In this work the behaviour of paints pigmented with the quoted metallic tannates and based on an epoxy binder was studied. The epoxy binder consisted of a base with a weight per epoxide WPE about 450 and a polyamineamide hardener with an amine value in the 210-220 range. The solvent mixture, expressed as % w/w, was 42.7 % xylene, 14.6 % butanol and 42.7 % oxygenated hydrocarbon. Clay modified with gel-like amines was added as rheological agent after finishing the pigment dispersion (1 % w/w on the coating).

2.3. Pigment level. Generally, the corrosion-inhibiting paints are formulated with a pigment volume concentration lightly less than the critical pigment volume concentration (CPVC), where just sufficient binder is present to fill the voids between the pigment particles [14].

CPVC was estimated by carrying out determinations of permeability of free films by applying the Gardner method [15]; the trials were made in triplicate, averaging the results

obtained. Afterwards, the experimental values were plotted in function of PVC considered, which ranged from 30.0 to 50.0 %, with increases in 5.0 % each time. To obtain CPVC the curves were adjusted to the polynomial equation $y = A + Bx + Cx^2 + Dx^3$ through a regression method and calculating the root of the second derivative (inflexion point). Experimental CPVC values ranged from 38 to 42 %. Finally, taking into account those results the PVC values were selected: 35.0 and 40.0 %.

3. Paint manufacture

It was performed at laboratory scale in triplicate by employing a porcelain jar ball mill of 1.0 liter of total capacity. Mill operative conditions were specially considered with the aim to achieve an efficient pigment dispersion [16].

Firstly, a solution of epoxy resin in the solvent mixture was prepared with stirring. The ball mill was loaded with the mentioned vehicle and the pigments were added; these components were milled for 24 hours previous incorporation of a dispersant in the quantity indicated by the manufacturer. After pigment dispersion, the rheological agent was added by employing a high speed agitation equipment .

The hardener was mixed with the base of the paint in the ratio suggested by the manufacture (2/1 epoxy resin/hardener ratio in weight) before its application.

4. Experimental tests

SAE 1010 steel plates of 150 x 80 x 2 mm were used for the tests. The plates were previously sandblasted to Sa 2 ½ (SIS Specification 05 59 00/67), with a 40 µm maximum roughness (Rm); then they were cleaned and coated with the experimental paints by brushing. A dry film thickness of 80 ± 5 µm was obtained; paints were applied with an interval of 24 hours between coats. Tests were performed at 20 ± 2 °C, seven days after the application of paints for curing.

4.1. Salt spray (fog) testing. Painted plates were exposed in a salt spray chamber adjusted to ASTM B 117: temperature 35 °C, continuous spraying with 5 % sodium chloride solution of pH 6.5-7.2 [17]. All panels were assessed for 500, 1000 and 1500 hour testing: degree of rusting according to ASTM D 610 was determined. Tests were carried out in triplicate and then mean values were calculated.

4.2. Film adhesion. A great number of tests are often used in an attempt to measure film adhesion; different methods would give very dissimilar values: they would depend on substrate/film interface size and shape, force application rate, test temperature, etc. In spite of the mentioned difficulties, it is possible to select a method to determine adhesion performance and to obtain relatively precise data by controlling those factors which influence the results: a known variation would lead to establish differences in performance. The Elcometer Tester Model 106 (ASTM D 4541) was used to determine adhesion on coatings after 1500 hours in salt spray chamber. Ten determinations at room temperature (20 ± 2 °C) were made to minimise the results scattering. The fracture values of the studied paints were expressed with

respect to the aged binder after 1500 hours in salt spray chamber ($80 \pm 5 \mu\text{m}$ dry film thickness).

4.3. 100 % relative humidity chamber. Other series of panels were placed in an enclosed chamber containing a heated, saturated mixture of air and water vapour according to ASTM D 2247. The surfaces were observed at 500, 1000 and 1500 hours of testing. The degree of blistering was evaluated by using ASTM D 714; blistering corresponded to the osmotic phenomenon, that is the blistering exclusively promoted by water diffusion through the paint film and not from rusting. This test was also made in triplicate.

RESULTS AND DISCUSSION

Typical properties of metallic tannates

Atomic absorption determinations permitted to assess the capacity of forming complex of condensed tannins in the used conditions. The values ranged between 2.0 and 2.5 % for iron and between 4.5 and 4.8 % for tin, both of them in weight on the corresponding metallic tannates.

Particles of metallic tannates showed a small mean size and in consequence a large specific area, Table I. These characteristics agree with the visual conclusion: precipitates are extremely fine and so they can not be retained in their totality by filter paper. Furthermore, microscopic observations allowed to determine some hydrophobic characteristics of the pigments, that is that the particles of both metallic tannates are repelled by drops of water.

Table I

Typical properties of metallic tannates

Property	Iron tannates	Tin tannates
Colour	Blue black	Light brown
Density, g.cm^{-3}	1.52/1.54	1.54/1.56
Oil absorption, g/100 g	20.4	20.3
Particle size (50.0/50.0 %), μm	2.9	2.7
Specific surface area, $\text{m}^2.\text{g}^{-1}$	1.2	1.3
Fe, % by weight	2.0-2.5	-----
Sn, % by weight	-----	4.5-4.8
Na, % by weight	0.6	0.1

Other properties of iron tannates and tin tannates are assembled in Table I. Figures 1 and 2 show the infrared spectrums corresponding to tin tannates and iron tannates, respectively. In both cases, the reduced absorption in $3400\text{-}3200 \text{ cm}^{-1}$ band corresponds to the remaining hydroxy phenolic groups of the original tannins.

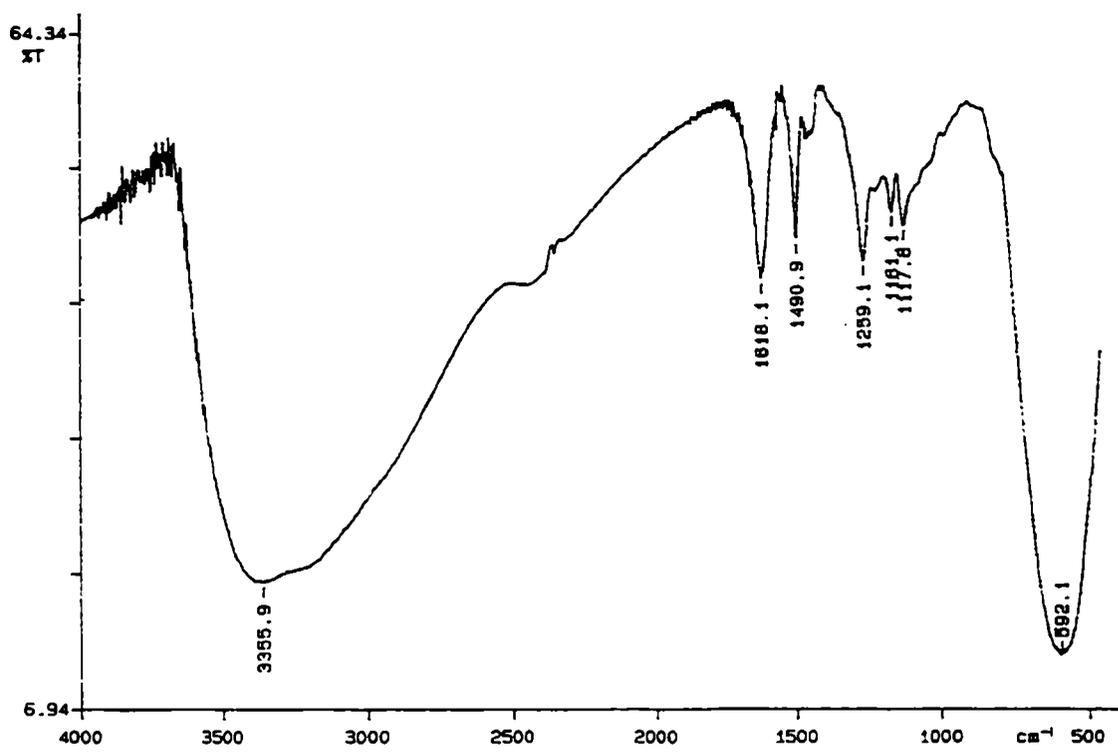


Fig. 1.- Infrared spectrum of tin tannates.

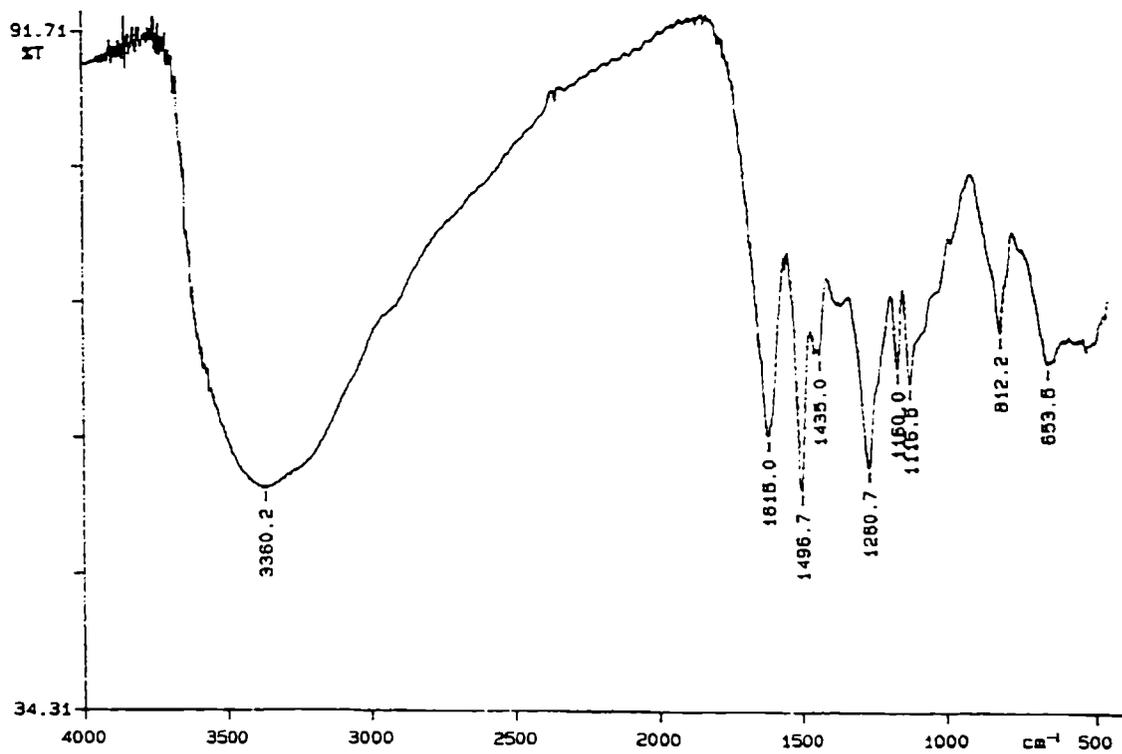


Fig. 2.- Infrared spectrum of iron tannates.

Degree of rusting and practical adhesion

The results obtained in salt spray testing (degree of rusting) and practical adhesion (tension of fracture) were statistically treated according to a factorial design of the 2 x 2 x 3 type (two pigments, two pigment volume concentrations and three inhibitive pigment/inert pigment ratios, that is 12 combinations); every combination included replicas. The values assembled in Tables II (degree of rusting) and III (practical adhesion) were used to calculate the estimated variance and afterwards the F test was carried out [18]. The tables mentioned [19] indicate that PVC and inhibitive pigment/inert pigment ratio (effects P and R, respectively) showed a meaningful influence on the paint behaviour while the type of inhibitive pigment (effect T) displayed an action devoid of significance.

Table II

**Salt spray (fog) testing (ASTM B 117)
Degree of rusting (ASTM D 610)***

Inhibitive pigment	Inhibitive pigment/ inert pigment ratio	PVC, %	Time, hours		
			500	1000	1500
Iron tannates	30/70	35.0	9	7	6
	40/60		10	9	8
	50/50		9	9	8
	30/70	40.0	9	8	8
	40/60		10	10	9
	50/50		10	10	9
Tin tannates	30/70	35.0	8	8	7
	40/60		9	9	7
	50/50		10	9	8
	30/70	40.0	10	9	9
	40/60		10	10	9
	50/50		10	10	9
Zinc tetroxychromate	30/70	40.0	9	9	8

* Key of the table: rust grade 10, no rusting or less than 0.01 % of surface rusted; 9, less than 0.03 % of surface rusted; 8, less than 0.1 % of surface rusted; 7, less than 0.3 % of surface rusted; 6, less than 1.0 % of surface rusted.

Table III**Practical adhesion, 1500 hour salt fog testing
(relative to aged binder)**

Inhibitive pigment	Inhibitive pigment/ inert pigment ratio	PVC, %	Fracture value, adimensional unit
	30/70	35.0	1.43
	40/60		1.64
	50/50		1.71
Iron tannates	30/70	40.0	1.68
	40/60		1.79
	50/50		1.82
Tin tannates	30/70	35.0	1.53
	40/60		1.60
	50/50		1.72
	30/70	40.0	1.77
	40/60		1.85
	50/50		1.83
Zinc tetroxyhromate	30/70	40.0	1.69

Note: Practical adhesion for original binder/aged binder ratio was 1.65

To interpret the experimental results corresponding to painted panels, the main effects were considered; the mean values of trials carried out in triplicate are shown in Table IV. These values indicate that to reach the best performance in salt spray testing for 1500 hours, of both inhibitive pigments (tin tannates and iron tannates), the 50/50 inhibitive pigment/inert pigment ratio and the 40 % pigment volume concentration must be selected. Considering the R effect, in order of importance to the 50/50 ratio, it is possible to quote the 40/60 ratio (similar effectiveness) and finally the 30/70 ratio. Concerning the P effect, the concentration 35 % was located in the following level to 40 %.

Degree of blistering

The results obtained in 100 % relative humidity testing (degree of blistering) could not be interpreted by means of the before mentioned statistical method since frequency of blistering

is not qualified in a quantitative manner by ASTM D 714 Standard in contrast to the size of blistering which is described in an arbitrary numerical scale from 10 to 0. The mean values for 500, 1000 and 1500 hours are shown in Table V.

Table IV
Mean values of degree of rusting and practical adhesion
(salt spray testing, 1500 hours)

	Type	Degree of rusting	Practical adhesion, adimensional unit
Inhibitive pigment	Iron tannates	8.00	1.68
	Tin tannates	8.17	2.73
Inhibitor/inert pigment ratio	30/70	7.50	1.60
	40/60	8.25	1.72
	50/50	8.50	1.77
Pigment volume concentration, PVC %	35	7.33	1.61
	40	8.33	1.79

Results corresponding to coated panels showed an apparent major tendency to blister in the composition in which the PVC value was 35 %; on the other hand, the blistering resistance improved at 40 % PVC with the both metallic tannates and for all the inhibitive pigment/inert pigment ratios selected.

The major tendency to blister at 35 % may be attributable to the inferior film permeability since this value increases as PVC also increases, particularly at pigmentation levels close to the critical one.

Regarding the type of metallic tannates and inhibitor/inert pigment ratios, no significant differences were observed.

CONCLUSIONS

- The testing results indicate that the iron tannates and tin tannates prepared at laboratory scale displayed a very good behaviour in accelerated tests like salt spray (fog) testing, 100 % relative humidity chamber (in both cases for 1500 hours) and practical adhesion on aged films (salt spray chamber, 1500 hours).

Furthermore, the quoted metallic tannates are not toxic and fulfil with the regulations in force in many countries over contamination and security.

- Both inhibitive pigments show a reduced solubility in water; the high blistering resistance corresponding to the osmotic phenomenon (that is not from rusting) could be attributable to this cause.

Besides, their low oil absorption (approximately 20 g/100 g) allows the incorporation of high levels of pigment in the formulation, with the advantage that this gives to this type of paints (simultaneous requirements of high rusting resistance, no blistering formation and adequate film practical adhesion).

Table V

**100 % relative humidity chamber (ASTM D 2247)
Degree of blistering (ASTM D 714)***

Inhibitive pigment	Inhibitive pigment/ inert pigment ratio	PVC, %	Time, hours		
			500	1000	1500
Iron tannates	30/70	35.0	8-F	8-M	7-M
	40/60		7-M	6-M	6-M
	50/50		8-M	8-M	7-M
	30/70	40.0	10	9-F	9-M
	40/60		9-F	9-F	8-F
	50/50		10	10	9-F
Tin tannates	30/70	35.0	8-F	8-M	7-M
	40/60		7-MD	6-MD	6-MD
	50/50		7-M	6-M	6-M
	30/70	40.0	10	10	9-F
	40/60		9-F	9-F	9-M
	50/50		10	9-F	9-M
Zinc tetroxychromate	30/70	40.0	9-F	8-M	8-M

* Key of the table. Size: 10, no blistering; 8, smallest size blister easily seen by the unaided eye; 6, 4 and 2 represent progressively larger sizes. Frequency: F, few; M, medium; MD, medium dense; D, dense.

• The pigment volume concentration and the inhibitor/inert pigment ratio performed a meaningful influence over the corrosion-inhibitive efficiency of paints based on metallic tannates. For both PVC considered, an increase of the inhibitor/inert pigment ratio led to a major anticorrosive efficiency; 40 % PVC improved the protective capacity of coatings.

•In spite of the scattering of the experimental results, it is possible to conclude that paints with low pigment content (35 % PVC) showed cohesive and adhesive failures; with a higher pigment content (40 % PVC) the failure was usually of the adhesive type.

• Coatings of major efficiency were formulated with a 40 % PVC value and a 30/70 v/v metallic tannates/inert pigment ratio. These coatings showed either a similar or a light superior behaviour to the reference sample based on zinc tetroxychromate.

•For a 6 month storage, metallic tannates incorporated to the epoxy base showed a very low sedimentation and a suitable can stability. After adding the curing agent, the corrosion-inhibiting coatings could be easily applied with only a previous light stirring.

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