

**WASH-PRIMERS FORMULATIONS FOR PAINTING
STEEL SUBSTRATES WITH POOR SURFACE PREPARATION**

Christian Byrne
Facultad de Ciencias Exactas, Universidad
Nacional de La Plata, CIDEPINT (Centro de
Investigación y Desarrollo en tecnología de
Pinturas)
Calle 52 e/ 121 y 122, sin n°
La Plata, Buenos Aires, B1900AYB
ARGENTINA

Oriana D'Alessandro
Facultad de Ciencias Exactas, Universidad
Nacional de La Plata, CIDEPINT (Centro de
Investigación y Desarrollo en tecnología de
Pinturas)
Calle 52 e/ 121 y 122, sin n°
La Plata, Buenos Aires, B1900AYB
ARGENTINA

Gonzalo J. Selmi
CICPBA, CIDEPINT (Centro de Investigación y
Desarrollo en tecnología de Pinturas)
Calle 52 e/ 121 y 122, sin n°

La Plata, Buenos Aires, B1900AYB
ARGENTINA

Roberto Romagnoli
CIDEPINT (Centro de Investigación y
Desarrollo en tecnología de Pinturas)
Calle 52 e/ 121 y 122, sin n°
La Plata, Buenos Aires, B1900AYB
ARGENTINA

Cecilia Deyá
Facultad de Ingeniería, Universidad Nacional
de La Plata, CIDEPINT (Centro de
Investigación y Desarrollo en tecnología de
Pinturas)
Calle 52 e/ 121 y 122, sin n°
La Plata, Buenos Aires, B1900AYB
ARGENTINA

ABSTRACT

The objective of this research was to formulate two wash-primers containing “quebracho” tannin and the corresponding lanthanum “tannate” derivative. The primers were applied on rusted steel and on cold rolled steel surface as they stand after the production process.

The primed panels were exposed to the humidity chamber to assess blistering and rusting degrees and adhesion by the cross cut test. The electrochemical evaluation was carried out by measuring the corrosion potential, the corrosion current density and the ionic resistance of the primed panels.

Results showed that the primers had good adhesion on the panels with poor surface preparation. During the exposure to the humidity chamber the primers did not blister. Steel corrosion was constrained in the case of the primer containing “quebracho” tannin.

Electrochemical tests showed that the wash-primers inhibited steel corrosion. As the primers do not possess barrier properties, corrosion inhibition is kinetic in nature by “quebracho” tannin and its

derivative. No significant differences were found between the primer pigmented with “quebracho” tannin and that containing lanthanum “tannate”.

Key words: Key words: wash-primer, SAE 1010 steel, “quebracho” tannin, adhesion, corrosion

INTRODUCTION

The corrosion of steel in contact with the atmosphere leads to oxide layers that make painting difficult and diminish paint performance [1, 2]. Besides, other problem in coating steel can be the low roughness of the substrate, when sanding is not possible. So, many studies were done in order to find protective coatings that can be applied on poor prepared substrates (oxidized or with low roughness) and that enhance the adhesion of the paint.

Tannins are polyphenolic compounds of vegetable origin that has been widely used as corrosion inhibitors of steel with controversial results. Several research works were done on the application of tannins on oxidized steel, tannins from mangrove (*Rhizophora apiculata*) [3], mimosa [4], pine [5], oil palm fruit [6] and “tara” (*Caesalpinia spinosa*) [7] were used. The presence of aromatic rings with hydroxyl groups in ortho positions made the tannin capable to form chelates with iron and other metallic cations. In the case of Fe^{+3} ion, a dark blue, highly insoluble complex, called ferric “tannate”, is formed [8-10]. In this way, a passive and adherent film that delays corrosion is formed and the application of tannins on oxidized steel became very promising.

In earlier research works, the precipitation of “tara” or “red quebracho” (*Schinopsis lorentzii*) tannins with a lanthanum salt was tested with good results [11, 12]. The protective action of these “lanthanum tannates” would have two contributions. On one hand, the effect of tannins and on the other hand, the pigment would slowly release little quantities of lanthanum on the surface, with the later formation of the very slightly soluble $La(OH)_3$. This precipitation occurs on cathodic areas due to the alkalization during corrosion.

The objective of this work was to study the temporary protection provided by “quebracho” tannin and its lanthanum derivative incorporated in coatings (primer) applied on steel poorly prepared, oxidized or low roughness substrate. A primer formulated with the traditional zinc tetroxychromate was used as control. The primers were studied by accelerated test (exposition to humidity chamber) and by electrochemical tests (corrosion potential measurements, ionic resistance and corrosion current density determination).

EXPERIMENTAL PROCEDURE

Preparation and characterization of metal substrates.

Commercial SAE 1010 steel panels (100 mm x 75 mm x 1 mm) were used as substrate.

Panels previously degreased with isopropyl alcohol were exposed in the humidity chamber (ASTM D 2247 [13]) for 20 days. These panels were dried for 24 h in laboratory air conditions ($20 \pm 2^\circ C$; RH 70%) before use.

Panels not exposed to the humidity chamber and only degreased with isopropyl alcohol were also employed. The total height of the roughness profile (Rt) of these panels, measured with a Hommel Tester T1000E, was 6 μm .

Preparation of lanthanum “tannates”.

The main solution of the tannin was prepared from the commercial powder of “quebracho” (UNITAN CROWN ATO). The powder was liquid-solid extracted for 1h with distilled water at $90^\circ C$. The extract obtained was vacuum filtered. KNO_3 1M was added as stabilizer.

In order to prepare lanthanum “tannate”, the extract was put in contact with $\text{La}(\text{NO}_3)_3$ 0.1M solution at pH=8, adjusted with NaOH 1M, under constant stirring for 1h. The precipitated obtained was washed with distilled water and dried at 100°C in oven for 24h.

Formulation, preparation and characterization of the primers.

The primers were formulated in two-pack system, to be mixed just before use in 4/1 A/B ratio, by weight. Pack A had the anticorrosive pigment (tannin, lanthanum “tannate” or zinc tetroxychromate, as control pigment), filler (talc), prime pigment (carbon black), resin (polyvinyl butyral, BUTVAR®), solvents (isopropyl acid and n-butyl alcohol) and water. The components of the Part A were dispersed in a 1L ball mill for 24 h to achieve an acceptable dispersion degree. Solvents (isopropyl acid and n-butyl alcohol) and citric acid were mixed to obtain Pack B. In this case, citric acid was used to replace the traditional phosphoric acid in order to avoid the precipitation of the insoluble lanthanum phosphate ($\text{pK}_{\text{sp}} = 27.92$) [14].

The steel samples oxidized in the humidity chamber were cleaned with a steel brush in order to remove the loosely oxides, then cleaned with isopropyl alcohol and sandpapered with n° 400. Finally, they were cleaned again with isopropyl alcohol and painted, using a brush, up to a final thickness of less than 10µm, measured with a Schwyz SC117-02 coating thickness gauge.

A group of non-oxidized steel samples were degreased with isopropyl alcohol and painted with the primers, as before.

The primed panels were kept under laboratory conditions for 4 days before testing.

The primer prepared with tannin was labelled as Q while the primer containing lanthanum “tannate” was labelled as QL. On the other hand, the substrates were labelled as O for the oxidized in the humidity chamber and D for the degreased non-oxidized ones. Zinc tetroxychromate primer was labelled as Z, ZO (for example) corresponds to samples of zinc tetroxychromate primer applied on oxidized steel (Table 1).

Table 1. Replicates’ nomenclature

Pigment		Substrate	
		Degreased (D)	Oxidized (O)
“Quebracho” tannin (Q)	Commercial	QD	QO
“Quebracho” lanthanum “tannate” (QL)	Q + $\text{La}(\text{NO}_3)_3$	QLD	QLO
Zinc tetroxychromate (Z)	Commercial	ZD	ZO
Steel without primer (blank, B)		BD	BO

Evaluation of the primers

The adhesion (ASTM D 3359 [15]) of the primers to the substrate was evaluated after curing and after the exposition in the humidity chamber.

Three of each primed panels were placed in the humidity chamber (ASTM D 2247 [13]) in order to evaluate the adhesion, the blistering degree (ASTM D 714 [16]) and the rusting degree (ASTM D 610 [17]) as a function of time. The degreased samples were removed after 5 days in the humidity chamber due to the important rusting degree while the oxidized samples were kept in for 7 days.

Electrochemical tests were done on delimited 3 cm² area with an acrylic cylinder, filled with NaCl 0.1 M, as electrolyte. The corrosion potential was measured employing a saturated calomel electrode. The ionic resistance was measured using a Pt counter-electrode and an ATI ORION model 170 conductivity meter, at 1000 Hz. The corrosion current density was determined by linear polarization (± 30 mV from open circuit potential) with a Gamry Interface 1000 potentiostat, employing the software Gamry Echem Analyst Version 6.33. A typical three electrodes cell (a Pt counter-electrode, a saturated calomel electrode as reference and the primed steel as working electrode) was used; the scan rate was

1 mV/s. As the primers possessed low ionic resistance, it was possible to determine the corrosion rates by the linear polarization method. Measurements were done during 50 days.

RESULTS

The adhesion of the primer, after curing, in the cases of QO and QLO was good, but in ZO, around 15-35 % of the painted was removed with the tape. In the cases of the degreased substrates, the adhesion was better, qualification 4B for QD and QLD and 5B for ZD (Table 2).

Humidity chamber

Neither of the samples presented blistered during the tests.

Oxidized substrate: the adhesion of the primers was poor after 1 day in the chamber, almost completely lost in the cases of QO and QLO.

The oxidation degree of the primed substrate diminished as a function of time, being QO protected as ZO. QLO, on the other hand, behaved poorly; the protection was completely lost after 3 days in the chamber (Table 2).

Degreased substrate: the adhesion of the primers to the degreased low roughness substrate was very good, but completely lost after 1 day. The loss was more abruptly than in the cases of the oxidized substrate. QD and ZD behaved similar after 5 days but afterwards, QD protection was completely lost. QLD, with lanthanum “tannate”, behaved similar to QLO (Table 2).

Table 2. Humidity chamber. Degree of Rusting and Adhesion by Tape Test

Replicates		Adhesion (ASTM D 3359)*					Degree of Rusting (ASTM D 610)#			
		Time (days)					Time (days)			
		0	1	3	5	7	1	3	5	7
Without primer	BO	-	-	-	-	-	1	0	0	0
	BD	-	-	-	-	-	0	0	0	-
“Quebracho” primers	QO	4B	2B	1B	1B	1B	9	7	7	3
	QLO	3B	2B	1B	1B	1B	6	4	4	3
	QD	4B	1B	1B	0B	-	8	7	4	-
	QLD	4B	1B	1B	1B	-	6	4	3	-
Zinc tetroxychromate primer	ZO	2B	2B	1B	1B	1B	9	8	6	4
	ZD	5B	1B	1B	0B	-	9	8	6	-

#Rusting degree	10	9	8	7	6	5	4	3	0
Rusted area %	0	0.01-0.03	0.03-0.01	0.1-0.3	0.3-1	1-3	3-10	10-16	>50

* % of the painted area removed: 5B. None; 4B: less than 5%; 3B: 5-15%; 2B: 15-35%; 1B: 35-65, 0B: greater than 65

Electrochemical studies

The ionic resistance values for the control panels (BD and BO) were very similar and around $200 \Omega \cdot \text{cm}^2$ along the whole essay, slightly lower than the values corresponding to ZO and ZD (Fig. 1). The ionic resistance's values of the panels with primers based on "quebracho" tannin (QD, QO, QLD and, QLO) were higher than the corresponding controls, being the differences about 2-4 times.

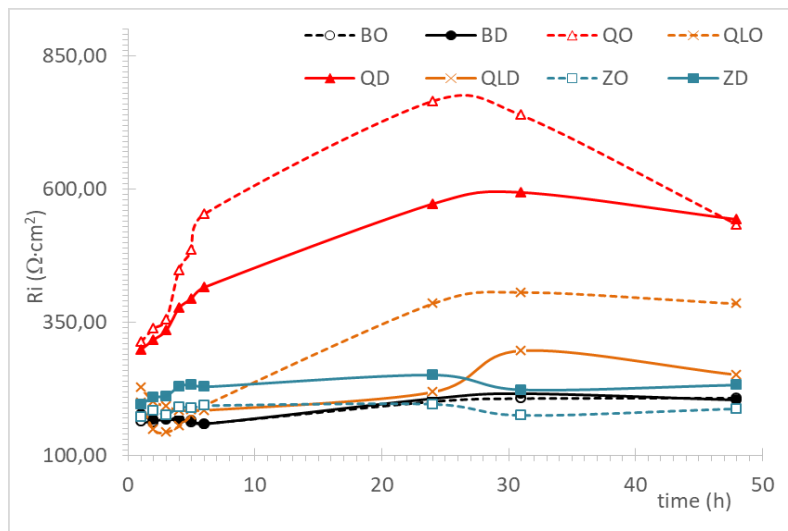


Figure: Ionic resistance of the panels

The corrosion current density (J_c) of the oxidized primed substrates were higher than that of the oxidized control, and around $25\text{-}30 \mu\text{A}/\text{cm}^2$. In the cases of the low roughness substrate all the samples had J_c values around $5\text{-}10 \mu\text{A}/\text{cm}^2$ during the essay.

Regarding the corrosion potentials values (E_c) all of them were depleted to more negative values during the first 5 days or immersion and then they kept constant for almost 50 days. After 144 days of immersion, E_c values of the controls, ZD and ZO were around -750 and -710 mV, respectively and the values corresponding to the "quebracho" tannin primers were around 100 mV more positives (Figure 2).

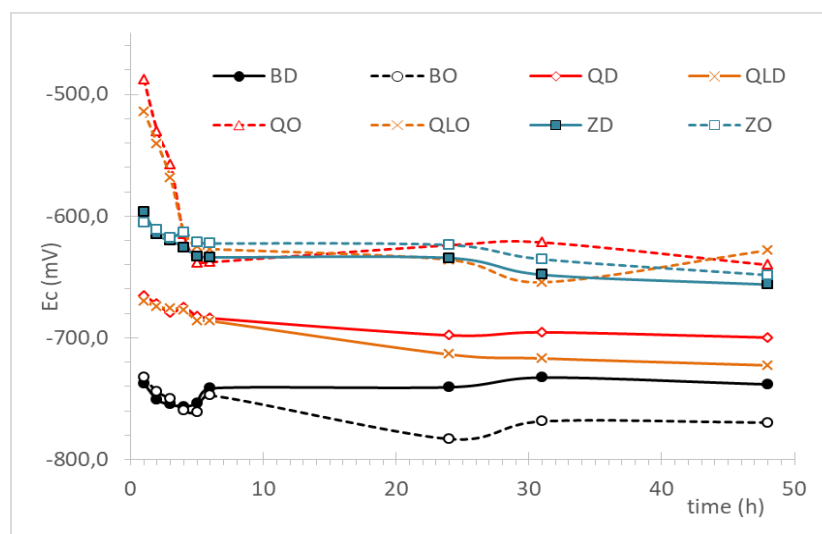


Figure 2: Corrosion potential of the panels

According to references [8-10], tannins can react with Fe^{+3} forming insoluble “iron tannate”, that precipitates on the substrate inhibiting further the reaction. This reaction enhances the protection of the primer and the adhesion to the substrate compared with traditional zinc tetroxychromate. In a future step, the tested primer would be included in a complete paint system (primer + anticorrosive paint + top coat) and test in accelerated and electrochemical assays to evaluate the performance of the protection.

CONCLUSIONS

Lanthanum “tannate” can be prepared employing “quebracho” tannins and lanthanum nitrate solution in order to be incorporated in a protective primer. This primer can be applied on low roughness steel or on oxidized panels with an adhesion similar to zinc tetroxychromate primers. The electrochemical tests showed the tannin and “tannate” primers had better barrier properties than zinc tetroxychromate one.

ACKNOWLEDGEMENTS

The authors thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de La Plata (UNLP), Departamento de Ingeniería Química and Comisión de Investigaciones Científicas of Buenos Aires (CICPBA), for the financial support of this research.

REFERENCES

- [1] B. N. Popov. Atmospheric Corrosion. In: Elsevier, editor. Corrosion Engineering 2015. p. 451-80.
- [2] J. Alcántara, B. Chico, I. Díaz, D. de la Fuente, M. Morcillo, “Airborne chloride deposit and its effect on marine atmospheric corrosion of mild steel”, Corrosion Science. 97 (2015) 74-88.
- [3] A. A. Rahim, M. J. Kassim, E. Rocca, J. Steinmetz, “Mangrove (*Rhizophora apiculata*) tannins: an eco-friendly rust converter”, Corrosion Engineering, Science and Technology 46 (2011) 425-31.
- [4] T. K. Ross, R. A. Francis, “The treatment of rusted steel with mimosa tannin”, Corrosion Science 8 (1978) 351-61.
- [5] G. Matamala, W. Smeltzer, R. Benevente, “Pine tannin rust converter for steel protection by painting”. CONAMET-SAM Conference, Concepción, Chile: Universidad de Concepción, 1989).
- [6] M. N. Mohamad Ibrahim, M. Y. Nor Nadiah, A. A. Amirue, “Extraction of Tannin from Oil Palm Empty Fruit Bunch as a Rust Deactivator”. Regional Symposium on Chemical Engineering (Hanoi, Vietnam, 2005), 197-201.
- [7] S. Flores Merino, J. J. Caprari, L. Vasquez Torres, L. Figueroa Ramos, A. Hadzich Girola, “Inhibitive action of tara tannin in rust converter formulation”, Anti-Corrosion Methods and Materials 64 (2017) 136-47.
- [8] J. Iglesias, E. García de Saldaña, J. A. Jaén, “On the tannic acid interaction with metallic iron”, *Hyperfine Interactions*, 134 (2001) 109-114.
- [9] J. A. Jaén, J. De Obaldía, M.V. Rodríguez, “Application of Mössbauer spectroscopy to the study of tannins inhibition of iron and steel corrosion”, *Hyperfine Interactions* 202 (2011) 25-38.
- [10] S. Yahya, A. M. Shah, A. A. Rahim, N. H. Abd Aziz, R. Roslan, “Phase transformation of rust in the presence of various tannins”, *Journal of Physical Science*, 19 (2008) 31-41.

- [11] O. D'Alessandro, G. Selmi, C. Deyá, A. De Sarli, R. Romagnoli, "Lanthanum Derivative from "Tara" Tannin for Steel Temporary Protection", *Industrial and Engineering Chemistry Research* 57 (2018) 3215-3226.
- [12] O. D'Alessandro, G. Selmi, C. Deyá, A. Di Sarli, R. Romagnoli, "Formulation and assessment of a wash primer containing lanthanum "tannate" for steel temporary protection", *Journal of Material Engineering and Performance*, 27 (2018) 687–704.
- [13] ASTM⁽¹⁾ D 2247 (2015), "Standard Practice for Testing Water Resistance of Coatings in 100% Relative Humidity" (West Conshohocken, PA: ASTM).
- [14] F. H. Firsching, J. C. Kell "The Solubility of the Rare-Earth-Metal Phosphates in Sea Water". *J. Chem. Eng. Data* 38 (1993) 132-133.
- [15] ASTM⁽¹⁾ D 3359 (2009), "Standard Test Methods for Measuring Adhesion by Tape Test" (West Conshohocken, PA: ASTM).
- [16] ASTM⁽¹⁾ D 714 (2002), ASTM International Standard test method for evaluating degree of blistering of paints (West Conshohocken, PA: ASTM).
- [17] ASTM⁽¹⁾ D 610 (2010), ASTM International Standard practice for evaluating degree of rusting on painted steel surfaces (West Conshohocken, PA: ASTM).

⁽¹⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

