



PERGAMON

Corrosion Science 43 (2001) 1003–1018

**CORROSION  
SCIENCE**

www.elsevier.com/locate/corsci

## Possible improvements in the action of some rust converters

C.A. Barrero<sup>a,b</sup>, L.M. Ocampo<sup>b</sup>, C.E. Arroyave<sup>b,\*</sup>

<sup>a</sup> *Solid State Group, Department of Physics, University of Antioquia, P.O. Box 1226, Medellin, Colombia*

<sup>b</sup> *Corrosion and Protection Group, Department of Materials Engineering, University of Antioquia, P.O. Box 1226, Medellin, Colombia*

Received 8 September 1999; accepted 17 July 2000

---

### Abstract

The anticorrosive properties of 18 rust converters were investigated. The corrosion products on pre-rusted mild steel samples and their mechanisms of reaction with the converters were studied. Accelerated corrosion tests were also performed. It was found that a mixture of tertbutyl and isopropyl alcohol facilitates penetration and adherence of the converters. Nevertheless, the converter does not reach the metal surface and the reactions are largely restricted to the outer layers. This circumstance, and the fact that anticorrosive properties are accelerated test-dependent, were considered as important reasons for the understanding of the contradictory results found with these products. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Rust converters; Tannic and phosphoric acids; Surface treatments; Corrosion products

---

### 1. Introduction

Rust converters are chemical formulations that can be applied to corroded surfaces causing their passivation and elimination of possible further attack after the application of a coating. However, it is not yet possible to find on the market a really satisfactory product since reported results on the protection efficiency are highly controversial. In fact, the difficulty lies in finding the appropriate components, their optimal concentrations, the proper time of reaction, and the appropriate conditions

---

\* Corresponding author. Tel.: +57-4-210-55-45; fax: +57-4-211-90-28.

E-mail address: carroyav@udea.edu.co (C.E. Arroyave).

for their most effective application, i.e., the nature of the rust to be converted (e.g. thickness, age of formation, composition), the most suitable painting system and the best atmospheric conditions for their application. In relation to the composition, it is well known that the most common rust converters are based on tannic and phosphoric acids. However, the results reported with respect to the anticorrosive properties and mechanisms of reaction are questionable [1,2]. Recently, it has been suggested that the type of tannin has a pronounced influence upon the anticorrosive properties of steel [3]. Several authors also suggest that the rust conversion using phosphoric acid solutions strongly depend on the acid concentration [4–6], in such a way that solutions containing between 15 and 33 wt.% in acid would be the ones offering the best results. Now, when both acids are present in the converter, the recommended concentrations differ from one work to another [7–10]. The time of reaction of the converters with the rust is another important factor [4,9,10]. Gust [9] found that the conversion time of lepidocrocite, magnetite and goethite into ferric tannate (in an aqueous solution of tannin 15%), were of three, over 6 and 12 months, respectively.

The type and concentration of alcohol used as a solvent, is another important factor, but very few works have been reported on this matter. It has been suggested that the mixture butyl and ethyl alcohol may increase the velocity of penetration of the converters into the rust layer [11]. It should also be considered that the crystalline oxides and the amorphous phases are more compact in comparison to the crystalline oxyhydroxides, which must affect the penetration depth of the converter [12–14]. On the other hand, Deslauriers [15] reported that the ability to prevent corrosion depends more on the rust layer thickness at the steel and on the barrier properties of the whole painting system, than in the ability of the formulations to convert the rust.

Up to now, only the components present in the converter and their concentrations have been reviewed. However, the composition of the rust layer and its time of formation at the corroded steel surface are other factors influencing the converter protection efficiency. It seems that the youngest rust reacts better with the converters, than the rust with considerable time of formation, because of its high reactivity. Moreover, the iron phases present in the rust react differently with the converter. It has been reported that magnetite reacts more rapidly with the acids than goethite, but much more slowly than lepidocrocite [9,10]. On the other hand, the atmospheric conditions, such as relative humidity and time of exposure affect considerably the degree of soundness of the rust and, consequently, the possibility of conversion [16].

The mechanisms of reaction for each acid with the most common iron phases have been reported in several works [6,9,10,17,18], providing a strong base for the correct interpretation of most of the results. However, there are still some issues that require more investigation [18]. In spite of the great quantity of published works, it is still required a product exhibiting adequate anticorrosive properties. In this work, it has been performed a detail study of the mechanisms of reaction and the protection efficiency of 18 different formulations of rust converters with the purpose to give more insight into this matter, looking for new more adequate products. The concentration of the tannic and phosphoric acids, and the type of alcohol are the main

variables considered. The effect of washing the converter before applying the coatings has also been considered.

## 2. Experimental procedure

A set consisting of 300 AISI SAE 1008 mild steel coupons with dimensions  $75 \times 150 \times 3 \text{ mm}^3$  were employed. The treatment applied to each coupon consisted in sandblasting until the “white metal” degree (SSCP SP-10) was reached and degreased with detergent, hot water, acetone and ethyl alcohol. Afterwards, the coupons were corroded to degree C (SIS 05 59 00, uniform attack) in a solution of 3.5 wt.% NaCl. Four of as such pre-rusted coupons were selected and analyzed using scanning electron microscopy (SEM), and by deep mechanical scraping the removed rust was studied by X-ray diffraction (XRD), and Fourier transform infrared (FTIR), and Mössbauer spectroscopies.

SEM analysis were performed in a Hitachi S-510 microscope working at 25 000 V and  $10^{-5}$  torr. This system has an instrumental resolution and covering of 70 and 120 Å, respectively. The samples were top coated with a very thin layer of 40% Au–60% Pd. FTIR spectra were collected in a Perkin-Elmer spectrometer operating in the transmission mode between 4000 and  $50 \text{ cm}^{-1}$ . KBr pellets in a relation 100/2 were employed. Room temperature (RT) Mössbauer spectra were obtained in the transmission mode using a constant acceleration drive and a triangular reference signal. A  $^{57}\text{Co/Rh}$  source with initial activity of 25 mCi was used. The spectra were adjusted using a program call MOSF [19,20]. The XRD measurements were performed on a Rigaku Miniflex diffractometer equipped with a  $\text{Cu(K}\alpha\text{)}$  radiation (50 kV and 10 mA), Ni filter and a proportional detector. The scans were done in the range of  $3\text{--}60^\circ$  ( $2\theta$ ), at  $2^\circ$  per minute.

The rust converters formulated in the present work were applied on the remaining corroded coupons and allowed to dry for eight days after application. The average thickness of rust plus converter was about  $108 \mu\text{m}$  for all coupons. The mechanisms of reaction of the rust with the converters were analyzed using the same procedure as previously described for the converters free corroded coupons. The remaining samples, which have been previously treated with the rust converters, were covered first with two coats of epoxy-phosphate primer, and then with two coats of epoxy-poliamida with total average thickness of 36.9 and  $50.2 \mu\text{m}$ , respectively. Some of these remaining coupons were previously washed before applying the coatings with the aim to eliminate the residual rust converter. Afterwards, for each formulated converter, four coupons (one washed, one with and two without incision) were always disposable to be submitted to the accelerated corrosion testing laboratory chambers.

Three types of corrosion tests were used: (i) alternating immersion/emersion tests in an aerated dissolution of 3 wt.% NaCl with a period of 48 h, (ii) exposition in a 100% humidity chamber (ASTM D 2247) and (iii) exposition in a chamber of salt fog (ASTM B 117). Along the tests, the degree of blistering (ASTM D 714) and corrosion (ASTM D 610) were evaluated. To all coupons the gloss (ASTM D 523),

adherence (ASTM D 4541) and chalking (ISO 4628-6) were measured before and after each test. At the end, the penetration of the corrosion was measured on the coupons with incision. The gloss was determined at an angle of 60° using a micro-TRI-gloss of GARDNER. The adherence measurements were performed on a hydraulic ELCOMETER 108.

An alphanumeric nomenclature of five characters was established to identify each coupon, as follows:

- First (test): A: alternating immersion/emersion; N: salt fog; H: humidity.
- Second (acid content): 1: 3T–30F; 2: 3T–35F; 3: 5T–30F; 4: 5T–35F; 5: 10T–30F; 6: 10T–35F. T and F mean tannic and phosphoric acids of analytical grade respectively. They were mixed in the weight percentage denoted by the corresponding numbers.
- Third (alcohol): P: isopropyl; B: tertbutyl; M: A 50–50% mixture of them.
- Fourth (washed): L: the coupon is washed; S: the coupon is not washed.
- Fifth (incision): I: sample with incision; O: sample without incision.

In order to code-name the coupons with just the applied rust converters, a nomenclature of two characters, involving only the second and the third of the mentioned ones, was used.

### 3. Results

#### 3.1. Scanning electron microscopy

Fig. 1 shows a typical photomicrograph of a rusted coupon without converter. The picture (a) shows a surface with fine grain (sandy type) morphology. The structure is also highly porous and presents cavities of different sizes. Besides these

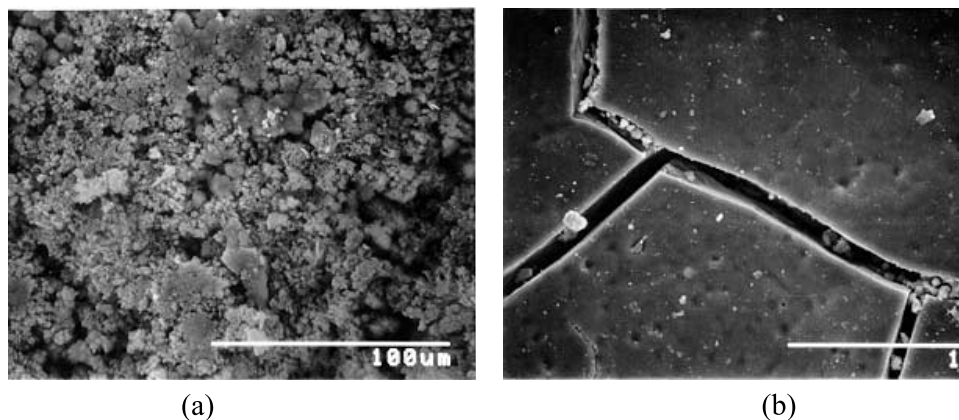


Fig. 1. Photomicrographs of the surfaces of (a) rusted sample and (b) sample 1M.

granular regions, it can also be observed regions of particles with the cactus shape. The first and second morphologies are indicative of the presence of lepidocrocite and traces of goethite, respectively [13]. The apparent major presence of particles with the granular morphology suggests a coupon surface dominated by lepidocrocite. It could not be observed the presence of magnetite at the surface, in spite of the fact that Mössbauer spectroscopy indicates that magnetite is the major iron phase present in the rust. It should be mentioned that in the scraping process, it was found an easy to remove layer at the top of the rusted coupon which had an orange color, and a relative more adherent layer close to the steel surface which had a black color.

The application of the formulated converters to the rusted steel surface forms an amorphous compact and cracked layer, with bulging and the presence of bright particles (Fig. 1(b)), in agreement with other reports [13,14]. These characteristics are common to all the studied coupons, differing only in their frequency and magnitude with which they are present. The bright particles show irregular shapes and different sizes. These particles can correspond to either residual converter or to some amorphous form of converted rust. In the picture of sample 1M, it is possible to see some grains that seems to emerge from the cracks, which can be associated to iron phases which could not be transformed by the action of the converter. The picture (b) also shows some dimples, whose origin can be due to the pressure the gas or water vapor exerts on the bulging until it burst as explained by Raman et al. [13]. In general, it has been observed that the greater the concentration of tannic acid is, the greater is the presence of bright particles, the less is the presence of dimples and the surface layer seems to be more compact.

### 3.2. Infrared spectroscopy

Fig. 2 shows the IR spectra of a typical rusted sample. It is possible to see (a) the bands at 1022 and 574  $\text{cm}^{-1}$ , which are the strongest bands of lepidocrocite and magnetite respectively. The two absorption lines at 889 and 793  $\text{cm}^{-1}$  give the characteristic “W” of goethite [21]. These lines are relatively broad, indicatives of goethite with poor crystallinity in agreement with the Mössbauer results. The broad bands in the range of 3000–3500  $\text{cm}^{-1}$ , can be assigned to the presence of a superficial adsorbed water and/or to OH vibrations [22].

The IR spectra in Fig. 2 of samples 1P (b), 1B (c) and 1M (d) suggest that lepidocrocite is perhaps the iron phase which more transformation to ferric phosphate has experienced. This is based on the fact that lepidocrocite's strongest band localized at 1022  $\text{cm}^{-1}$ , seems to be greatly transformed into a broad and noticeable band at 1044  $\text{cm}^{-1}$ , which is typical of ferric phosphate [9,10]. In contrast with lepidocrocite, the presence of magnetite cannot be discarded, because the band at 542  $\text{cm}^{-1}$  can be the result of a superposition of magnetite and ferric phosphate. A similar reasoning could be perhaps given to the small amount goethite, whose typical bands can be hidden by the strong and broad ferric phosphate bands. This interpretation is perhaps in agreement with the results reported by Gust [9] and Nasrazadani [10] who found that the phosphoric and tannic acids react more rapidly with lepidocrocite, a little slower with magnetite, and much slower with goethite. It is

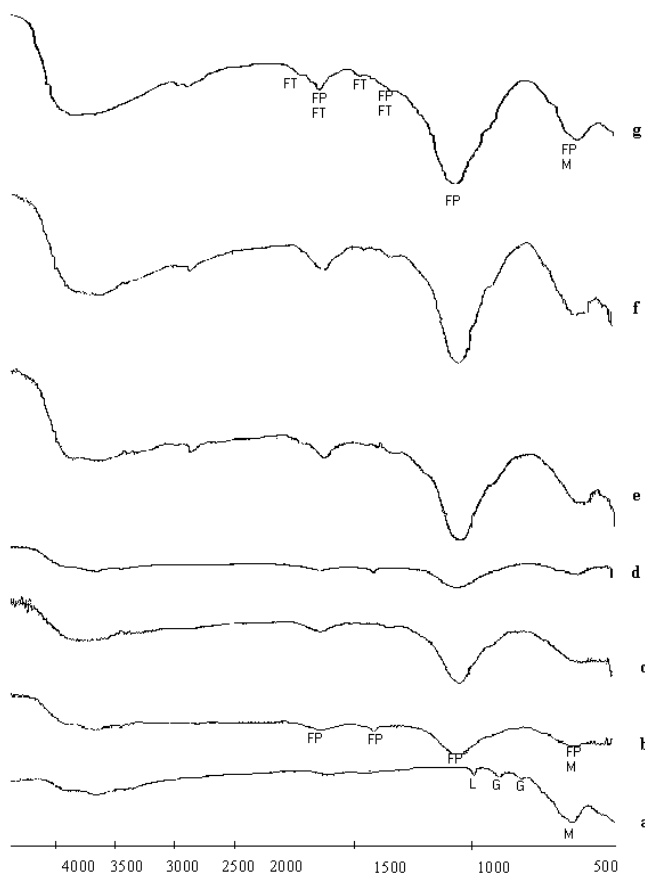


Fig. 2. Infrared spectra of samples: (a) rusted, (b) 1P, (c) 1B, (d) 1M, (e) 2P, (f) 2B, (g) 2M. The absorption bands belonging to ferric tannate FT, ferric phosphate FP, goethite G, lepidocrocite L and magnetite M are indicated on some spectra.

interesting to note that the bands typical of ferric tannates, which are described below, are not clearly observable, suggesting that at these acid concentrations (3% tannic and 30% or 35% phosphoric), the different iron phases have been transformed mostly into ferric phosphate.

The intensity ratio of the ferric phosphate band at  $1044\text{ cm}^{-1}$  and the magnetite plus ferric tannate band at  $542\text{ cm}^{-1}$  shown in Fig. 3, is greater in the IR spectra of sample 6M (m), which contains 10%T, 35%F and mixed alcohol, than in sample 6P (k), which consist of 10%T, 35%F, and isopropyl alcohol. On the other hand, the shoulders at both sides of the broad  $1633\text{ cm}^{-1}$  band, which correspond to traces of ferric tannates, are more apparent in 6M than in 6P. The same observations can be deduced when spectra of samples 6B and 6M or other pair of similar samples are compared. These results can be explained if it is surmised that the mixture of alcohol as compared to tertbutyl or isopropyl alcohol facilitates a deeper penetration of the

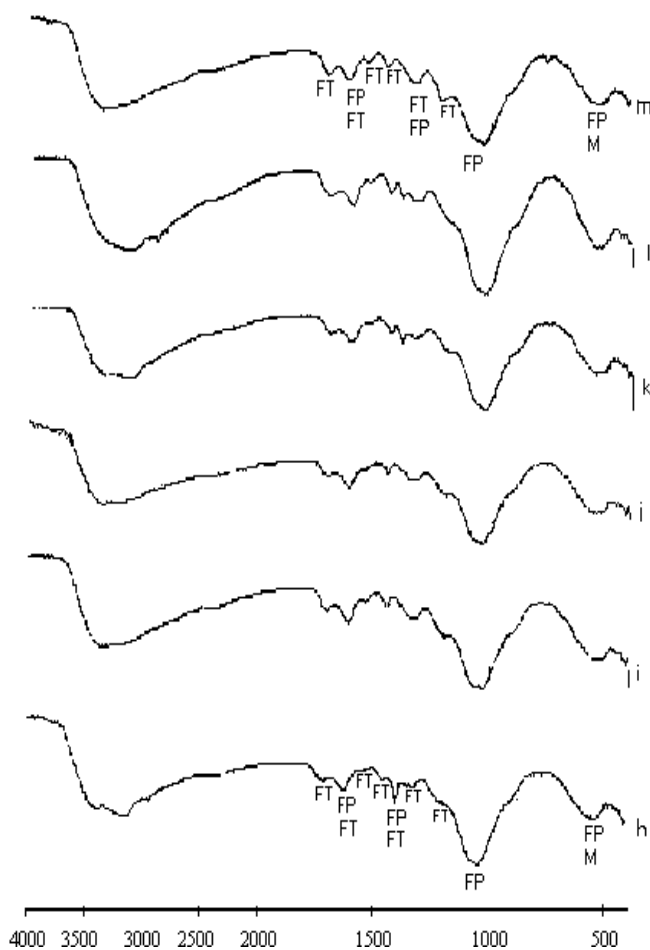


Fig. 3. Infrared spectra of samples: (h) 5P, (i) 5B, (j) 5M, (k) 6P, (l) 6B, (m) 6M. The absorption bands belonging to ferric tannate FT, ferric phosphate FP, and magnetite M are indicated on some spectra.

converter (mainly the tannic acid) into the rust layer, thus provoking more transformation of the rust. This interpretation is in agreement with the work by Gonzales and Corvo [11], who found a greater velocity of penetration of the converters when a mixture of ethanol and butanol are employed.

Fig. 3 shows that the increase in tannic acid concentration makes that the ferric tannate bands localized at about  $1540$  and  $1710\text{ cm}^{-1}$  start to be noticed. In fact, as expected, these bands are more pronounced in the formulation numbers 5 and 6 (10% tannin) than in numbers 1 and 2 (3% tannin). By comparison of the IR spectra of samples 2B (Fig. 2(f)) and 6B (Fig. 3(l)), it is observed that the  $1615\text{ cm}^{-1}$  band is due to the contribution of both ferric phosphate and ferric tannate. The band at  $1728\text{ cm}^{-1}$  clearly indicates the presence of ferric tannate. In spite of this, the ferric

phosphate bands were always relatively more intensive than the tannate ones in all samples. This is an indication that in the proposed formulations the majority of the iron phases in the rust are transformed into ferric phosphates than in ferric tannates.

### 3.3. Mössbauer spectroscopy

Mössbauer spectra for all the samples were acceptably adjusted using two sextets and one doublet. The derived parameters are listed in Table 1. In the rusted sample, the two sextets exhibited parameters, which are typical of magnetite. The deviation of the ideal 1.8 value for the area ratios of A and B sites suggest that magnetite is either not stoichiometric, that exhibits poor crystallinity or that a substitution of iron for an alloying element has happened [23]. On the other hand, the hyperfine parameters of the doublet recommend either the presence of one iron oxyhydroxide of poor crystallinity or a mixture of some of them. In fact, these compounds are goethite of poor crystallinity and lepidocrocite as found using the other techniques. Additionally, the area values show that magnetite is the most abundant among the iron phases present in the rust.

As already mentioned, the spectra of the samples with converter were also adequately adjusted with two sextets and one doublet. The two sextets were again attributed to magnetite, which also exhibits a deviation of the ideal 1.8 value in the  $A_B/A_A$  area ratio. It has been determined the amount of  $^{57}\text{Fe}$  in magnetite transformed by the action of the converter in relation to the amount of  $^{57}\text{Fe}$  in magnetite present in the rusted sample. These values, which are called the converted fraction CF, are listed in Table 1. If it is assumed that the Mössbauer  $f$  factors are similar to all the iron phases present, then the CF values indicate that only between 7% and 24% of the  $^{57}\text{Fe}$  in magnetite has been transformed by the action of the rust converters. Considering the experimental errors, these results means that an important portion of the magnetite remains without conversion.

The doublet, present in the spectra of the samples with converter, has been attributed to the overlapping contributions coming from goethite of poor crystallinity, ferric tannate and ferric phosphate. All of these compounds exhibit similar Mössbauer parameters at RT, making difficult their identification using this technique [17,23,24]. Any attempt to incorporate two or more doublets representing the presence of these compounds resulted in no fitting improvement and at the contrary it introduced meaningless values. It has been reported that with RT Mössbauer spectroscopy it is not possible to test the chemical nature of the transformation suffered by the rust due to the action of the converters [24], and this is confirmed with the present results. Perhaps measurements at lower temperatures can provide additional information (see for example the work by Favre et al. [18]). These measurements are in progress.

### 3.4. X-ray diffraction

The XRD pattern of the rusted sample, i.e., before application of the converter, shows the presence of magnetite, small amounts of lepidocrocite and traces of



Table 1  
Parameters obtained from the RT Mössbauer spectra for some selected samples

Sample	Sextets							Doublet		
	$\chi^2$ <sup>a</sup>	$H_A$ <sup>b</sup> (kOe)	$H_B$ <sup>b</sup> (kOe)	$\delta_A$ <sup>c</sup> (mm s <sup>-1</sup> )	$\delta_B$ <sup>c</sup> (mm s <sup>-1</sup> )	$A_B/A_A$ <sup>d</sup>	CF <sup>e</sup> (%)	$\Delta E_Q$ <sup>f</sup> (mm s <sup>-1</sup> )	$\delta^g$ (mm s <sup>-1</sup> )	$A^h$ (%)
Rusted	1295	487	454	0.27	0.60	1.06	–	0.65	0.35	30
1P	1268	488	457	0.29	0.56	1.81	16	0.65	0.36	41
1M	1160	488	460	0.29	0.57	1.76	17	0.58	0.35	42
2P	1181	489	460	0.30	0.63	1.85	19	0.68	0.38	43
2M	1353	487	453	0.29	0.57	1.46	16	0.58	0.37	41
3P	1287	489	452	0.30	0.55	1.74	10	0.63	0.35	37
3M	1207	485	461	0.24	0.61	0.94	14	0.62	0.38	42
4P	1111	487	449	0.30	0.56	1.41	7	0.60	0.37	35
4M	1179	486	462	0.28	0.60	1.04	24	0.62	0.36	47
5P	1344	489	458	0.30	0.57	2.16	14	0.57	0.38	40
5M	1142	486	456	0.33	0.58	1.37	9	0.62	0.37	36
6P	1079	488	458	0.28	0.60	1.50	14	0.58	0.37	40
6M	1185	489	460	0.28	0.60	1.68	16	0.60	0.35	41

<sup>a</sup> Chi-square for 1024 points.

<sup>b</sup> Hyperfine field for the A and B sites respectively.

<sup>c</sup> Isomer shift relative to  $\alpha$ -Fe at RT for the A and B sites, respectively.

<sup>d</sup> Area ratio of the A and B sites.

<sup>e</sup> The <sup>57</sup>Fe fraction present in magnetite that has been converted by the action of the acids, relative to the amount of <sup>57</sup>Fe in magnetite present in the rusted sample.

<sup>f</sup> Quadrupole splitting.

<sup>g</sup> Isomer shift.

<sup>h</sup> Area occupied by the doublet.

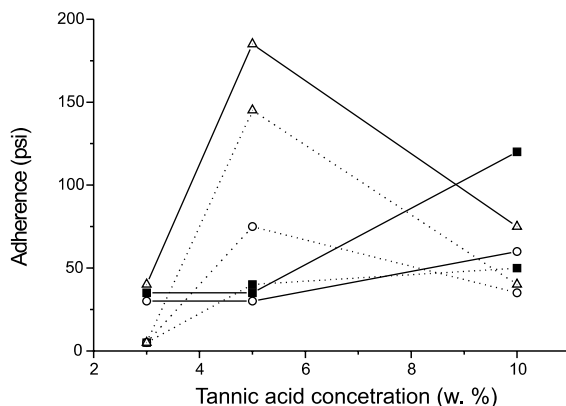


Fig. 4. Variation of the adherence with the concentration of tannic acid. The solid and dotted lines represent the converters with 35 and 30 wt.% in phosphoric acid respectively. The filled squares, the open circles and the open up triangles represent the formulations based in isopropyl, butyl and their mixture, respectively.

goethite, as found by the other techniques. The patterns of the samples with converter show again the presence of magnetite, as revealed by the other techniques, and traces of goethite. However, no indications of lepidocrocite could be detected presumably because it has been converted to ferric phosphate/tannate.

### 3.5. Coating characteristics

It has been found that the gloss measurements were in the range between 22 and 37, whereas the chalking was very similar to all the samples with a value of 2. Fig. 4 shows the behavior of the converters adherence to the corroded surface. In general, the formulations exhibiting the better adherence are based in the mixture of alcohol with the major concentration of phosphoric acid and intermediate concentration of tannic acid. This result coincides with the fact that the greater Mössbauer CF value is observed for sample 4M (see Table 1). Besides, the better adherence of the converters based in the mixture of alcohol is in agreement with the deeper penetration of these converters into the rust layer as found by FTIR measurements. In fact, it is expected that the greater the penetration is, the greater is the adherence of the converter.

### 3.6. Accelerated corrosion tests

The rusted coupons treated first with the converters and afterwards with the whole painting system were subjected to accelerated tests of corrosion with the purpose to check for anticorrosive properties. Table 2 and Fig. 5(a), Fig. 5(b), and Fig. 5(c) show the results for the alternating immersion/emersion (*A*) tests performed on some selected samples. It seems that the best results against the corrosion pro-

Table 2

Averaged results of the final evaluations performed on some coupons exposed to the alternating immersion–emersion tests

Coupon	Corrosion progress <sup>a</sup> (mm and/or %)	Blistering <sup>b</sup> (ASTM D 714)
A1PSO	80%	8D
A1PLI	1 mm, 15%	2MD
A1PSI	6 mm, 20%	2MD
A2PSO	50%	4M
A2PLI	3 mm, 10%	2MD
A2PSI	4 mm, 30%	4MD
A3PSO	80%	8D
A3PLI	6 mm, 30%	2MD
A3PSI	4 mm, 20%	4MD
A4PSO	55%	PN
A4PLI	50%	2MD
A4PSI	5 mm, 15%	4MD
A5PSO	10%	6D
A5PLI	20%	2MD
A5PSI	3 mm, 10%	4MD
A6PSO	50%	PN
A6PLI	50%	8D
A6PSI	4 mm, 10%	4D
A1MSO	40%	2M
A1MLI	10 mm, 30%	2M
A1MSI	11 mm, 20%	2M
A2MSO	40%	PN
A2MLI	6 mm	2MD
A2MSI	7 mm	2MD
A3MSO	3%	PN
A3MLI	8 mm	2MD
A3MSI	4 mm, 15%	2MD
A4MSO	17%	PN
A4MLI	7 mm, 20%	4MD
A4MSI	7 mm, 15%	2MD
A5MSO	50%	8D
A5MLI	3 mm, 4%	2MD
A5MSI	5 mm, 3%	2MD
A6MSO	50%	8D
A6MLI	2 mm, 14%	2MD
A6MSI	2 mm, 3%	2MD

<sup>a</sup> Percentage of the area rusted according to the photographic reference standards (ASTM D 610), and the penetration distance from incision, in mm.

<sup>b</sup> Blistering frequency: dense D, medium dense MD, medium M, few F. Blistering size: 10 represents no blistering, 8 represents smallest size blister, 6, 4 and 2 represent progressively larger sizes.

gress and blistering appears to be given by the formulations 5 and 6, which correspond to higher acid contents, based in the mixture of alcohol. It can also be deduced that in most of the formulations, the procedure of washing the converter with water does not produce any noticeable improvement in the anticorrosive properties.

Table 3 and Fig. 5(d), Fig. 5(e), and Fig. 5(f) show the results of the evaluations in the 100% humidity chamber (*H*) for some selected samples. In contrast to the results

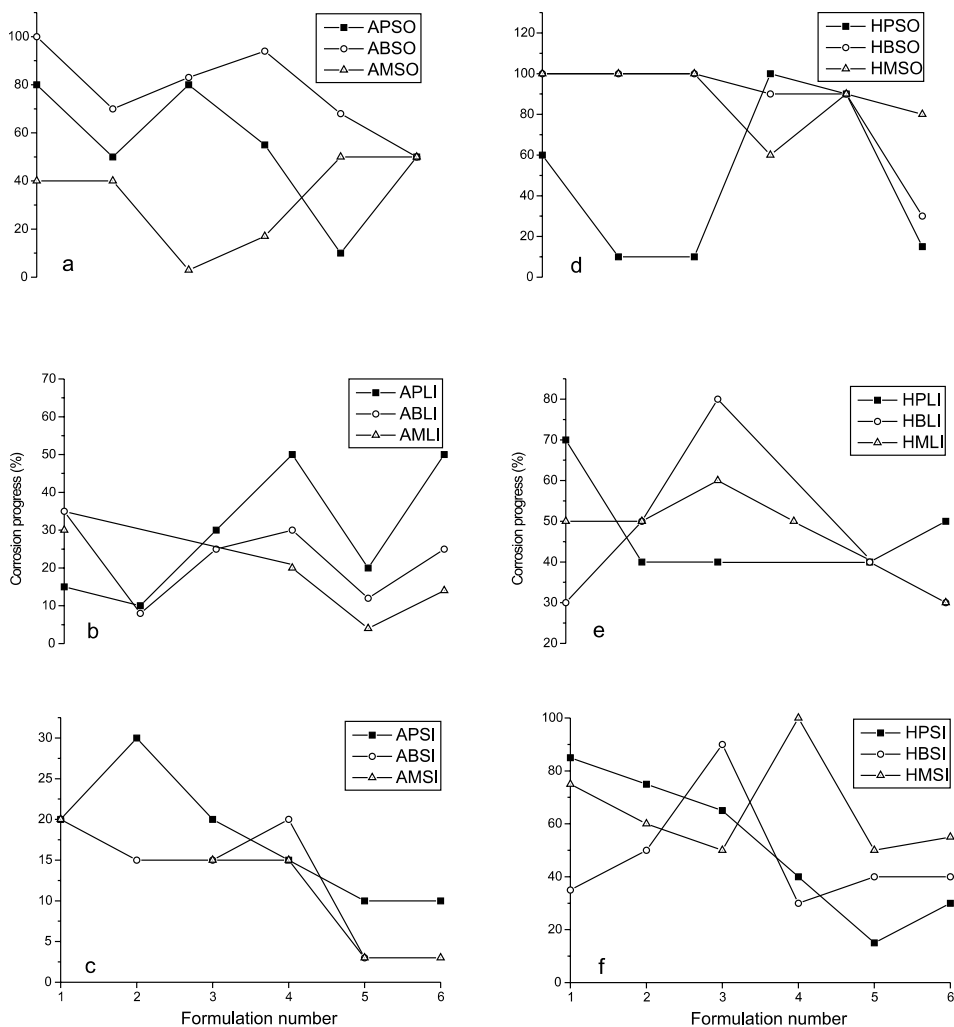


Fig. 5. Variation of the corrosion progress for some selected coupons as a function of the converter's formulation number. These coupons were exposed to the immersion-emersion tests (a, b and c) and to the humidity chamber (d, e, and f). The filled squares, the open circles and the open up triangles represent the formulations based in isopropyl, butyl and their mixture, respectively. The solid lines are drawn to guide the eyes. The nomenclature used in the figure is the same as that in the text.

obtained with the *A* tests, the better behavior against the corrosion progress are exhibited by the formulations based in low or very high concentrations of both acids and in isopropyl alcohol. However, as found for the *A* tests, the procedure of washing the converter is not justified in the great majority of cases, because it does not generally improve the anticorrosive properties. This latter result is also common to the salt fog (*N*) tests. These results suggest that the anticorrosive behavior of the

Table 3

Averaged results of the final evaluations performed on some coupons exposed to the 100% humidity chamber

Coupon	Corrosion progress (mm and/or %)	Blistering	Gloss
H1PSO	60%	PN	20(5)
H1PLI	70%	6MD	–
H1PSI	85%	4MD	10(1)
H2PSO	10%	4MD	16(3)
H2PLI	40%	4M	–
H2PSI	75%	4MD	8(2)
H3PSO	10%	PN	20(5)
H3PLI	40%	4M	–
H3PSI	65%	4MD	13(3)
H4PSO	100%	PN	24(2)
H4PLI	6 mm	2MD	–
H4PSI	7 mm, 40%	4D	7(2)
H5PSO	90%	PN	25(7)
H5PLI	40%	4M	–
H5PSI	3 mm, 15%	2D	11(3)
H6PSO	15%	4MD	23(5)
H6PLI	50%	2D	–
H6PSI	3 mm, 30%	2D	15(2)
H1MSO	100%	PN	21(5)
H1MLI	50%	4D	–
H1MSI	75%	2D	13(1)
H2MSO	100%	PN	27(5)
H2MLI	50%	2M	–
H2MSI	60%	2MD	15(3)
H3MSO	100%	6MD	22(7)
H3MLI	60%	4D	–
H3MSI	8 mm, 50%	2MD	19(3)
H4MSO	60%	2MD	19(3)
H4MLI	3 mm, 50%	4MD	–
H4MSI	100%	2D	14(3)
H5MSO	90%	4M	15(4)
H5MLI	5 mm	4MD	–
H5MSI	1 mm, 50%	4D	19(6)
H6MSO	80%	PN	16(2)
H6MLI	1 mm, 30%	2D	–
H6MSI	55%	2D	13(2)

Conventions as in Table 2. Ratio of the reflected to the incident light fluxes in a sample determined at an angle of 60°. Numbers in parentheses represent the errors in the gloss measurements.

converter depends upon the accelerated test performed, and that the procedure of washing the converter is not generally justified in all the performed accelerated tests.

On the other hand, the great majority of values for the corrosion progress through the incision was concentrated between 3% and 40% for the *A* tests, between 30% and 90% for the *H* tests, and between 40% and 100% for the *N* tests. These results seems to suggest that the protection against corrosion progress through the incision is greater in the *A* tests, intermediate in the *H* tests and poorer in the *N* tests.

On the other hand, it is found that the lost of final gloss is greater in the *H* tests than in the *N* ones, because these values were concentrated in the range between 7 and 27 for *H* and between 12 and 37 for *N*. As mentioned in Section 3.5., the initial gloss values were found to vary between 22 and 37. The lost of the final value with respect to the initial one for each test, demonstrate the lost in the stability of the coatings.

#### 4. Discussion

The results suggest that the corrosion products are accommodated in at least two layers: one relatively compact inner layer close to the steel surface, which is dominated by magnetite, and a second less compact outer layer, which is dominated by lepidocrocite. Poorly crystalline goethite is perhaps distributed among both layers. Upon the application of the converters both acids penetrates into the rust layers and react with the iron phases to produce ferric tannates and ferric phosphates films.

The major presence of phosphoric acid in all the formulations provokes that most of the iron phases transform into ferric phosphates. The characterization methods suggest that the reaction of the different iron phases with the tannic acid form only mono-complexes of the catecholade mode [17]. These reactions take place mainly at the outer layer, and to a lesser extent in the inner layer, i.e. the converters can not fully penetrate both layers. This latter statement is based on the finding in the Mössbauer work that the magnetite, which as already mentioned forms the inner layer, is largely unaffected by the converter.

The outer less compact layer, predominantly lepidocrocite, is transformed easier, and the inner one, more impermeable and inert, remains without reaction, according to the reported behaviors [9,10]. On the other hand, the initial transformation increases the outer layer impermeability, adding a new barrier for the expected converting effect.

Apparently, the latter situation is strongest with tannate, but phosphoric acid and alcohol help to increase penetration. The acid contributing to the configuration of a less impermeable transformation barrier and the alcohol by dissolution of the tannate.

There might remain excess of acids that would not react with the iron phases and form the bright particles. Nevertheless, its effect is not noticeable, as a consequence of the low protective capacity of the whole barrier.

At the end, was obvious that composition is an important factor on the transformation results, and the exposure conditions also play a significant role, explaining some contradictory reported results, and justifying a proposal on non-universal converters.

It is evident that further research on this complex matter is required. For example, it is still to discern the effect of several converter formulations on the different corrosion degrees and on the nature of the rust to be converted (e.g., age of formation, composition, thickness, etc.). In relation to the converter composition, it seems important to determine with most precision the percentage of isopropanol with re-

spect to tertbutanol, which are presented in the mixture of alcohol, that gives a better penetration of the acids.

## 5. Conclusions

The application of the different rust converters upon the corroded steel surface creates a compact, amorphous and cracked superficial layer, with bulges and the presence of bright particles. The converters transform the rust into ferric tannates and ferric phosphates, with a major presence of the latter. However, most of the rust can not be transformed, suggesting that the action of the converters is mainly superficial. The results suggest that the mixture of isopropanol and tertbutanol facilitates a deeper penetration and hence a better adherence of the whole coating system and that it should be consider in an optimal formulation. It has been found that the protective action of the converters is different for each test, justifying some of the contradictory results from the literature, and supporting the idea of specific converters, in agreement with the exposure conditions to be experimented.

## Acknowledgements

Authors thank Mr. Sergio Peñaranda the help provided in the sample preparation, and to the referees for valuable comments on the manuscript. The financial support given by the Committee for the Development of Investigation, CODI, at the University of Antioquia is greatly acknowledged.

## References

- [1] M. Morcillo, S. Feliu, J. Simancas, J.M. Bastidas, J.C. Galvan, S. Feliu Jr., E.M. Almeida, *Corros. NACE* 48 (12) (1992) 1032.
- [2] J.C. Galván, S. Feliu Jr., J. Simancas, M. Morcillo, J.M. Bastidas, E. Almeida, S. Feliu, *Electrochim. Acta* 37 (11) (1992) 1983.
- [3] L. Sorinas, F. Luzardo, T. Ochoa, E. Caraballo, A. Cabezas, L. Vargas, M. Garcia, *Corrosão e Protecção de Materiais* 16 (2) (1997) 6.
- [4] A.N. Nigam, R.P. Tripathi, K. Dhoot, *Corros. Sci.* 30 (8/9) (1990) 799.
- [5] E. Almeida, D. Pereira, J. Waerenborgh, J.M.P. Cabral, M.O. Figueiredo, V.M.M. Lobo, M. Morcillo, *Progr. Org. Coat.* 21 (1993) 327.
- [6] E. Almeida, D. Pereira, M.O. Figueiredo, V.M.M. Lobo, M. Morcillo, *Corros. Sci.* 39 (9) (1997) 1561.
- [7] Z.E. Alvarez, I. Callozo, D. Valdés, *Rev. Iber. Corros. Prot.* XVIII (1) (1987) 35.
- [8] M.I. Gonzáles, R. López Planes, *Rev. Iber. Corros. Prot.* XIX (6) (1988) 374.
- [9] J. Gust, *Corros. NACE* 47 (6) (1991) 453.
- [10] S. Nasrazadani, *Corros. Sci.* 39 (10–11) (1997) 1845.
- [11] M.I. Gonzáles, F. Corvo, *Rev. Iber. Corros. Prot.* XVIII (1) (1987) 39.
- [12] A. Razvan, A. Raman, *Pract. Met.* 23 (1986) 223.
- [13] A. Raman, S. Nasrazadani, L. Sharma, A. Razvan, *Pract. Met.* 24 (12) (1987) 577.
- [14] S. Nasrazadani, A. Raman, *Prac. Met.* 28 (6) (1991) 295.

- [15] P.J. Deslauriers, *Mater. Perfor.* 26 (1987) 35.
- [16] J. Gust, J. Bobrowicz, *Corros. NACE* 49 (1) (1993) 24.
- [17] J. Gust, J. Suwalski, *Corros. Sci.* 50 (5) (1994) 355.
- [18] M. Favre, D. Landolt, K. Hoffman, M. Stratmann, *Corros. Sci.* 40 (4/5) (1998) 793.
- [19] C.A. Barrero, Ph.D. Thesis, University of Gent, Belgium, 1997.
- [20] R.E. Vandenberghe, E. De Grave, P.M.A. de Bakker, *Hyperfine Interact.* 83 (1994) 29.
- [21] A. Raman, B. Kuban, A. Razvan, *Corros. Sci.* 32 (12) (1991) 1295.
- [22] R.M. Cornell, U. Schwertmann, *The Iron Oxides – Structure, Properties, Reactions, Occurrences and Uses*, VCH, Weinheim, 1996, p. 573.
- [23] R.E. Vandenberghe, E. De Grave, C. Landuydt, L.H. Bowen, *Hyperfine Interact.* 53 (1990) 175.
- [24] J.R. Gancedo, M. Gracia, W. Francisco, M. Morcillo, S. Feliu, *Hyperfine Interact.* 46 (1989) 461.