ISSN : 0974 - 7486 Volume 14 Issue 7

Materials Science

An Indian Journal

Full Paper

MSAIJ, 14(7), 2016 [255-266]

Corrosion protection assessment of nanoparticulate pre-treated galvanized steel/paint systems subjected to accelerated tests

C.I.Elsner[1, 2], P.R.Seré[1, 2], F.Martins Queiroz[3], C.R.Tomachuk[4], A.R.Di Sarli[1]*

[1]Cidepint: Research and Development Centre in Paint Technology (CICPBA-CONICET La Plata); Av. 52 s/n entre 121 y 122. CP. B1900AYB, La Plata, (ARGENTINA)

[2]Engineering School, National University of La Plata, Av. 1 Esq. 47. CP. B1900TAG, La Plata, (Argentina),

[3]Energy and Nuclear Research Institute, IPEN/CNEN-SP, CCTM, Av. Prof. Lineu Prestes, 2242, CEP 05508-000, São Paulo, SP, (BRAZIL)

[4]Engineering School of Lorena of the University of São Paulo (EEL-USP), Environmental and Basic Sciences Department, Estrada do Campinho s/n, CEP 12602-810, Lorena, SP, (BRAZIL)

E-mial: ardisarli@cidepint.gov.ar; cielsner@ing.unlp.edu,ar; mq_fernanda@yahoo.com.br; celiatomachuk@usp.br

ABSTRACT

The development of environmentally friendly anticorrosive systems providing the same performance than those already existing has been the great challenge for researchers working in the surface treatment field. In this work the corrosion behavior of two electrogalvanized-steel/nanoparticulate pretreatment/organic coating systems exposed to salt spray, controlled humidity and temperature, Prohesion or weathering chambers was studied. The global analysis of the obtained results allowed concluding that the protective behavior of both duplex systems was satisfactory, and that the nanoparticulate pretreatments based on trivalent chromium (Cr^{3+}) and Zirconium could be considered as a valid alternative to substitute those based on hexavalent chromium (Cr^{6+}). © 2016 Trade Science Inc. - INDIA

KEYWORDS

Electrogalvanized steel;
Conversion coatings;
Duplex systems;
Corrosion;
Paint.

INTRODUCTION

Clean technologies are features of the new millennium and involve the development of technologies that protect the environment throughout the production chain to eliminate the generation of pollutants “from raw material to finished product packaging and transportation”. For this, the technological sector has made huge efforts to increase productivity and reduce costs in business through: 1) effluents treatment; 2) use of a support system for the replacement of raw materials; 3) improvement in the production process, seeking minimization of pollutant generation; 4) reduction of the generated rejects; 5) recycling, involving the industrial design of eco-friendly products; and 6) join-efforts to transform the industrial areas into environmentally favorable ones.

Cr^{6+}-based compounds have been widely used in metal finishing and to provide corrosion protection to the metal surface of electronic equipments in the aircraft, food and automotive industries. In these industries, steel sheets are treated with chromate-based conversion coatings to provide good adherence to the paint system applied for protection and aesthetic purposes. However, Cr^{6+}-based compounds are classified as carcinogenic substances; moreover, as highly acid solutions that generate hazardous gases and have highly oxidizing characteristics are used during the production process, the effluents treatment process becomes economically unviable due to increasingly stringent limitations imposed by environmental legislations[1-4]. Currently, import restrictions on products containing hexavalent chromium have been imposed by the EE.UU and the EU, reason by which increasing international efforts are being made to develop reliable alternatives to this type of compounds.

Despite the use of Cr^{6+} in the chromatation bath is still allowed[5] there is a tendency, especially evident in Europe, Japan and USA, who are always closely following ecological aspects, to restrict the use of Cr^{6+}-based compounds. The development of novel eco- friendly surface treatments providing the same performance to those currently used represents a major challenge for those who investigate in the surface treatment field. In this sense, alternatives to the use of Cr^{6+} is of major importance[6-8], particularly considering the use of Cr^{3+} salts as the most viable alternative[9-15]. It has been shown that Cr^{3+}-based passivation coatings produce less-toxic materials compared to the Cr^{6+} ones, however, the corrosion resistance of those has not been comparable to the Cr^{6+} coatings[16, 17]. Attempts have been carried out to improve the corrosion resistance of the Cr^{3+} passivation coating. According to Fonte et al, the addition of transition metal ions such as Co^{2+}, Ni^{2+}, Fe^{2+} in the bath showed higher corrosion resistance than those formed in a bath without transition metal ions[17-19]. As well, some of the new chemical conversion treatments products based on silica, titanium and zirconium have shown promising results when applied to aluminum alloys or galvanized steel, even though their corrosion behavior is not as good as the obtained with traditional chromate surface treatments.

The aim of this work is the study of the corrosion behavior of electrogalvanized steel/ nanoparticulate pretreatment/organic coating systems subjected to accelerated exposure tests in Weathering, Salt Spray, Controlled Humidity and Temperature, or Prohesion Chambers. Electrochemical Impedance Spectroscopy (EIS) measurements, complemented with visual inspections and assessments of the coatings deterioration level (blistering, corrosion, loss of adhesion, loss of gloss and color, etc.) accomplished according to international standards were periodically used for checking the protective systems performance.

EXPERIMENTAL DETAILS

Materials

The test panels were AISI 1010 steel plates (15 x 7 x 0.1 cm) industrially electrogalvanized using a cyanide-free alkaline bath containing Zn^{2+} (12.5 g/L), KOH (170 g/L), K_2CO_3 (50 g/L), additive (10 mL/L), brightening agents (1 mL/L), and conditioner (10 mL/L). The following conditions were used: temperature (23±3 °C) and cathodic current density of 2 A/dm^2 for 45 min.

Prior to zinc coating, all the steel plates were degreased in a sodium silicate-based alkaline solution at room temperature, by applying a current density of 4 A/dm^2 for 3 min for improving the surface wettability. The samples were rinsed in deionized water, activated in an ammonia bifluoride 5% solution for 30 s, and rinsed again with deionized water.

Immediately after the electrogalvanising step, the sample surface was activated in a 0.5% HNO_3 solution (pH 1) for 10 s, and then, rinsed with deionized water. Subsequently, the surface was passivated using the following treatment:

Conversion coating preparation

The applied nanoparticulate pretreatment based on Cr^{3+} and Zr^{4+} was prepared using chromium trivalent salt, zirconium complexes (fluorzirconato de potassium) and potassium borate-fluoride, pH 4.2 (adjusted with 1% NaOH or 5% H_2SO_4 solutions), immersion time for 30 s at room temperature (23±3 ºC) with mechanical stirring.

Paints application on pretreated electrogalvanised steel samples

The pretreated (GSP) samples were then coated

TABLE 1 : Main characteristics of the formulated paints

Paint	Resin/Hardener (relationship)	Solvent	Pigment	PVC (%)
Polyurethane$_{solv}$ (SB)	Polyester/Aliphatic Isocyanate (4/1)	Xylene/methyl isobutyl ketone	TiO_2 (Rutile)	10
Polyurethane$_{aq}$ (WB)	Polyester/Aliphatic Isocyanate (4/1)	Water	Red Ferrite	10

TABLE 2 : Thickness of the tested paint films (µm)

Sample	System	Color	SSC	HC	WC	PC
GSP-SB	GSP/solvent-base paint	white	168±10	165±10	163±10	176±10
GSP-WB	GSP/waterborne paint	ochre	176±10	160±10	152±10	179±10

with paints designed, formulated, prepared and applied in the CIDEPINT laboratory, TABLE 1. For this, and leaving a 24 h drying period in between, two successive layers of a white solvent-based polyurethane paint pigmented with TiO_2 (GSP-SB samples), or an ochre waterborne polyurethane paint pigmented with red ferrite (GSP-WB samples) were applied by manual brushing. In the case of the WB paint, the "flash-rusting" effect was avoided by incorporating in its formulation a $NaNO_2$ solution (0.1% $NaNO_2$ on total paint). Both paints were formulated according to pigment volume concentration (PVC) = 10, particle size distribution from 0.1 to 10 µm checked by the ASTM D1210-05 standard, and a Pigment Volume Balance (Λ = PVC/CPVC (critical pigment volume concentration)) = 0.55). The painting systems were allowed to cure for 7 days at room temperature before starting the tests.

Dry film thickness was measured by an Elcometer mod. 300, using a bare electrogalvanized steel sheet as reference and pattern films with known thickness, TABLE 2.

Painted panels, prior to exposure, had a longitudinal scratch manually scribed through the tested coating using a carbide tip scribe making sure that the coating was scribed all the way through and into the substrate.

Performance tests

Accelerated tests

Corrosion behavior of the systems exposed in salt spray SSC (ASTM B117), Prohesion PC (ASTM G85–A5), weathering WC (ASTM G155–05a) or controlled humidity and temperature HC (ASTM D2247) chambers was periodically assessed by visual inspections and also as follows:

Physicochemical tests

Adhesion

Adhesion measurements were carried out by the Tape Test method according to the ASTM D3359-09e2 standard (Test Method B).

Gloss and color

Were respectively determined according to the ASTM D523-08, and the ASTM D2244-09b standards by using the BYK Gardner Spectro-Guide Sphere Gloss with 60 ºC of incidence angle.

Blistering and white rusting degrees

The size and frequency of blisters as well as the white rusting degree were evaluated according to the ASTM D-714-02 and ASTM D-610/08 standards, respectively.

Electrochemical tests

The shielding performance of each coating applied on the steel sheets and subjected to continuous immersion in open to air 0.5 mol/L NaCl (pH 6±0.3) solution or distilled water was periodically evaluated by EIS measurements. These were carried out using a conventional electrochemical cell with the three-electrode arrangement: a Pt-Nb mesh with negligible impedance acting as counter electrode (CE), a Saturated Calomel Electrode (SCE) as reference electrode (RE), and was the coated steel sample, placed horizontally looking upwards at the bottom in a flat-cell configuration, as working electrode (WE). The electrolytes were confined in a cylindrical clamp-on acrylic (polymethyl methacrylate) cell positioned on the WE by an O-ring defining a nominal testing area = 15.9 cm^2. All the measurements were performed at room temperature (22±3 ºC).

Impedance spectra in the frequency range $10^{-2} < f\,(Hz) < 10^5$ were obtained, in the potentiostatic mode at the free corrosion potential (E_{corr}), as a function of the immersion time in the electrolyte solutions using a Solartron 1255 FRA® coupled to an Impedance Potentiostat-Galvanostat EI® Solartron 1286 and both controlled by the ZPlot® program. The rms width of the sinusoidal voltage signal applied to the system was 8 mV and 10 points per decade were registered. The experimental spectra were fitted to model equivalent electrical circuits by using the Boukamp software[20], and the circuit components were associated to physicochemical process occurring in the system. All impedance measurements were performed with the electrochemical cell inside a Faraday cage to reduce external interferences as much as possible. The samples integrity was checked by measuring the corrosion potential after all the tests to confirm that the change from the initial value was no higher than ± 5 mV.

Taking into account that the corrosion behavior of passivated, painted and/or multi coated materials strictly depends on the production procedure; all the tests were carried out on three replicates of each sample type. The experimental results reported in the following Tables and Figures are the average of those obtained in each case.

RESULTS AND DISCUSSION

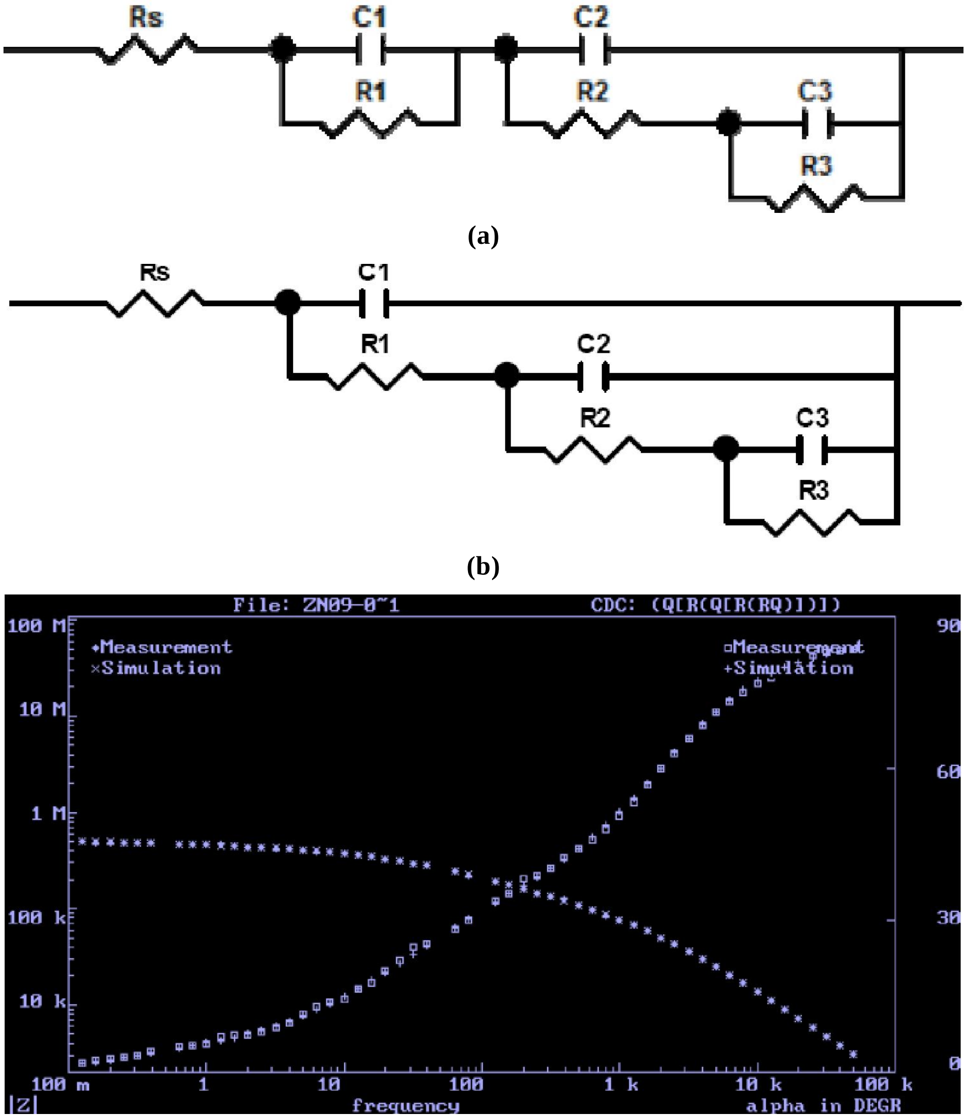
As a general hypothesis, it is assumed that the application of a pretreatment on the coated steel surface improves the metal/paint adhesion as well as the completely anticorrosive performance. In addition, if the applied painting system is the appropriate one, the formed duplex protective system will have a synergistic effect. All these concepts have been the objective of several exhaustive studies and have generated the development of highly satisfactory anticorrosive systems based on solvent-based paints. However, strict regulations designed to protect the environment and the public health increasingly prohibit the use of these products. Therefore, the need to replace them by others providing the same or even better performance requires new and accelerated studies. For this reason, the aim of this study is to assess the corrosion behavior of two electrogalvanized steel/paint film systems exposed to the action of several environments with different aggressiveness levels. A significant amount of experimental data gathered from standardized tests and electrochemical techniques are shown and analyzed with the purpose of determining a correlation with the physicochemical processes that are supposed to occur at an interface that is as complex as impossible to visualize by non-destructive means.

Impedance data deconvolution

One of the most important difficulties for analyzing the electrochemical impedance data from the impedance spectra deconvolution is, in general, to find an electrical equivalent circuit model and/or the parameters needed to explain the corrosion behavior of each analyzed system.

The electrochemical response of the GSP-SB or GSP-WB samples to an applied small AC potential perturbation could be modeled with the “most probable”[20] equivalent circuits - (a) whether the diffusional paths from the electrolyte to the zinc were aligned through the paint + pretreatment films, or (b) if, as is much more likely, these paths are not - shown in Figure 1.

In this, the first time constant (R_1C_1) appeared at the highest frequencies and represents the resistance to the ionic flux in the pores (R_1) and the dielectric capacitance (C_1) of the paint film. As the frequency values diminished, and taking into account that the permeating and corrosion-inducing chemicals (water, oxygen and ionic species) reach the nanoparticulate pretreatment, the second time constant (R_2C_2) represents the resistance to the ionic flux in the pores (R_2) and the dielectric capacitance (C_2) of the conversion layer. If the exposure time goes on, at lower frequencies can occur that the permeating reactants attain the electrochemically active zinc layer through the coating pores characterized by R_2, therefore, it is reasonable to assume that the corrosion process developing at the zinc surface should be placed in series with R_2. The R_3 and C_3 parameters account for the charge transfer resistance and the electrochemical double layer capacitance of the



(c)

Figure 1 : a) and b) equivalent circuits used to model the GSP-SB or GSP-WB samples exposed to HC or SSC for 42 days; and c) example of Bode plot displaying the measured and simulated (using the equivalent circuit shown in Figure 1 (b)) impedance data

corrosion process, respectively[22].

All the time constants exhibited some Cole-Cole type dispersion which had the corresponding n_i parameter, being $0 < n_i$ d” 1. Furthermore, distortions observed in those resistive-capacitive contributions indicate a deviation from the theoretical models in terms of a time constant distribution. Such deviations could be the result of either lateral penetration of the electrolyte at the substrate/coating interface (usually started at the base of intrinsic or artificial coating defects), underlying metallic surface heterogeneities (topological, chemical composition, surface energy), and/or diffusion processes feasible of occurring along the test. Since all these factors cause the impedance/frequency relationship to be non-linear, they are taken into consideration by replacing one or more capacitive components (Ci) of the equivalent circuit transfer function by the corresponding constant phase element (CPE_i), for which the impedance may be expressed as[23-25]:

$$Z = \frac{(j\omega)^{-n}}{Y_0}$$

Where; $Z(\omega) \Rightarrow$ impedance of the CPE ($Z = Z' + jZ''$)(Ω); j $\Rightarrow$ imaginary number ($j^2 = -1$); $\omega \Rightarrow$ angular frequency (rad)

$n \Rightarrow$ CPE power: ($n = \alpha/(\pi/2)$; $\alpha \Rightarrow$ constant phase angle of the CPE (rad); $Y_0 \Rightarrow$ part of the CPE independent of the frequency (Ω^{-1})

Difficulties are sometimes found in providing an accurate physical description of the occurred processes. In such cases, a standard deviation (χ^2) $\leq$ 5.10^{-4} was used as final criterion by considering that the smaller this value, the closer the fit to the experimental data[20]. In the present work, the fitting process was mainly performed using the phase constant element (CPEi) instead of the dielectric capacitance Ci. However, this last parameter was used in the following plots in order to facilitate the results visualization and interpretation.

Exposure in salt spray chamber

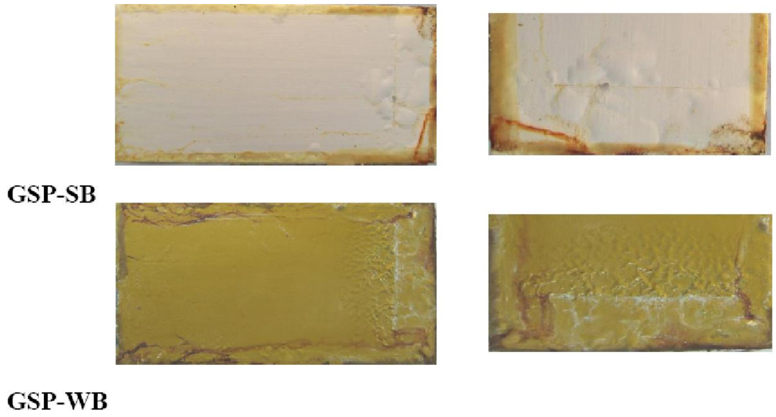
The SSC test is widespread in industrial practice and is certainly interesting, but this data could be quite rough and greatly affected if they are evaluated by different operators. On the other hand, EIS has been proposed as a useful tool for assessing the corrosion resistance.

Electrogalvanized steel sheets, which were pretreated and coated with the developed solvent-based or waterborne paints, were exposed in a salt spray chamber by duplicate for 42 days, performing periodic sampling to assess the coatings protective ability as well as their deterioration level.

Figure 2 shows the samples final state. In general, no blistering and/or corrosion were observed in the intact area of the samples while close to the cut there was an increasing blistering propagation with exposure time.

TABLES 3, 4 and 5 exhibit a summary of the obtained results. TABLE 3 illustrates that, in both systems, the dry adhesion was highly satisfactory, but also that a slight decrease (from 5B to 3B) of this property with the exposure time took place in the GSP-SB system; as well, an important detachment from the scratch was observed in both systems after 42 d of exposure, TABLE 4. Furthermore, TABLE 5 shows the color and gloss results obtained using a BYK Gardner reflectance photometer in accordance with the ASTM D 2244 and ASTM D 523 standards; also the following parameters: L: luminosity (white ≡ 100 and black ≡ 0); a and b: hue and saturation, mixing primary colors; and G: gloss. As can be seen, the organic coating did not display gloss or color variations in any of the exposed systems.

All the measured corrosion potentials (E_{corr}) values (Figure 3) showed a fluctuating behavior ranging from -0.75 to -1.02 V(ECS) indicating that, at initial stages of exposure, the zinc was poorly reactive due to the organic coating protection. However, as the exposure to the medium went on, the corrosion-inducing species such as water, oxygen and Cl^- ions permeated the paint film, reached the underlying zinc layer and, as a result, increased its electrochemical activity displacing the E_{corr} values towards more negative ones. Then, as the amount of zinc corrosion products was enough for sealing the paint defects, the increase of the coating barrier effect caused a diminishing of the zinc dissolution process and, consequently, the E_{corr} values became more posi-



(a) (b)

Figure 2 : Final condition of the samples after the exposure in the SSC; (a) global view and (b) detail of the incision area

TABLE 3 : Adhesion in the intact area before and after exposure in SSC

Sample	0d	42d
AGP-SB	5B	3B
AGP-WB	5B	5B

TABLE 4 : Detachment from the scratch as a function of the exposure time in SSC

Sample	15d	29d	42d
GSP-SB	0 mm	6 mm	25 mm
GSP-WB	0 mm	5 mm	23 mm

TABLE 5 : Color and gloss evaluation as a function of the exposure time in SSC

Sample	Exposure time											
	0d				1d				42d			
	L	a	b	G	L	a	b	G	L	a	b	G
GSP-SB	97.1	0.61	2.49	28.0	97.1	0.61	2.49	28.0	97.1	0.61	2.49	28.0
GSP-WB	59.2	16.3	46.6	76.9	59.2	16.3	46.6	76.9	59.2	16.3	46.6	76.9

L: luminosity (white ≡ 100; black ≡ 0); a and b: chromaticity coordinates (hue and saturation mixing the primary colors); G: gloss

tive. This is a process that is cyclically repeated until trial completion.

The impedance measurements performed in both systems showed a slow deterioration of the protection system, as seen in the evolution of the module of impedance (|Z|) and the phase angle (theta), Figure 3. In general, terms, both systems presented at least three time constants, the first one related to the organic film, while the other two were associated to the complex processes occurring at the zinc/paint interface.

In the GSP-SB system, the ionic resistance (R_1) of the organic film, related to the offered barrier effect, showed increasing values (10^6 -10^8 Ωcm^2) during the first 20 days of exposure with a subsequent decreasing trend, reaching values of approximately 10^5 Ωcm^2 towards the end of the test. In general, this type of evolution is interpreted by attributing the increase of the system impedance to the sealing effect given by the corrosion products gathered at the bottom and/or within the coating defects. However, this positive effect is overcome by the deterioration level of the protective coating, that is, blistering and/or swelling and/or delamination and/or generation of new defects due to the growing pressure exerted by the above mentioned products whose volume increases with hydration. In such circumstances, a decrease in |Z| values indicates the reduction of the barrier effect provided by the paint and the subsequent deterioration of its protective ability.

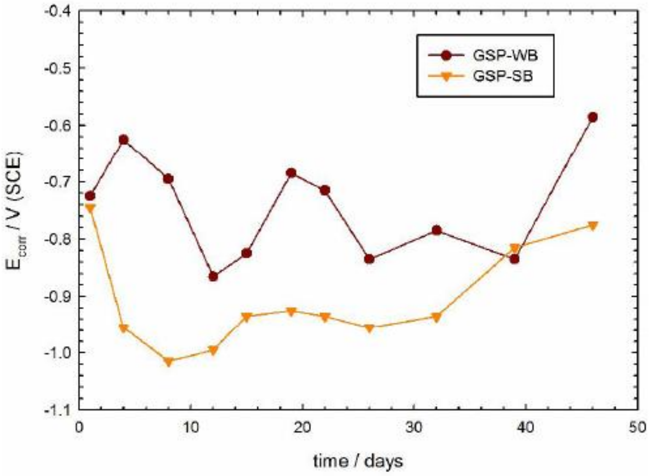
In the GSP-WB system, the ionic resistance of the paint showed a decreasing trend with the exposure time, fluctuating its value from 10^8 to 10^6 Ωcm^2. In this case, apart from the structural and crosslinking differences between both formulations, the above mentioned influence of the corrosion products which was initially positive, could not be observed due to the fact that the mechanical resistance of the waterborne paint to the deformation is highly lower than that exhibited by the solvent-based paint. For this reason, the deterioration rate acted much more rapidly.

Regardless the evolution of the system total impedance values, when the impedance deconvolution was done, and the resistive and capacitive components of the transfer function derived from the "more probable equivalent circuit"[20] were calculated, an important conclusion could be drawn. Even though in both systems an incipient corrosion process was detected from the first sampling, its evolution might be estimated as very slow since the charge transfer resistance values, which are inversely proportional to the corrosion rate, were in the order of 10^8 Ωcm^2.

Exposure in controlled humidity and temperature chamber

Replicates of the panels mentioned in the previous section were exposed in HC for 42 days. Sampling conditions and evaluation methodology were equivalent to that previously reported. Figure 4 shows the samples final state, while Figure 5 and TABLES 6-8 display the electrochemical and standardized tests results, respectively.

In general, the intact area of each sample (Figure 4) showed slight signs of blistering, which was classified according to the ASTM D 714 standard, TABLE



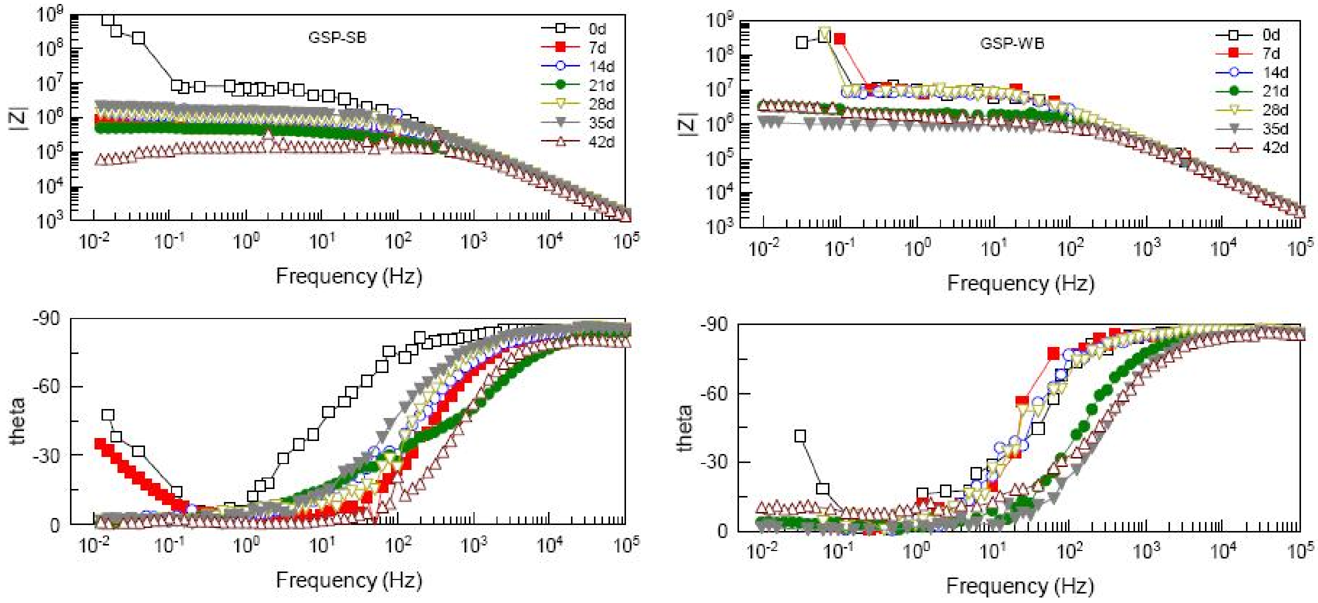


Figure 3 : Evolution of |Z| and (theta) as a function of the exposure time in the SSC

6. The zone close to the incision line did not show blistering but slight signs of corrosion were observed in the GSP-SB system.

The adhesion loss at the paint/zinc interface (TABLE 7) may be attributed to the breaking of the physical, mechanical and/or chemical bonds between the paint layer and the zinc surface. This effect, known as "wet adhesion", has been related to the reordering in the polymeric film structure due to the pressure[21] and strongly dielectric character of the absorbed water. This character makes that the water acts as a plasticizer able to modify the intermolecular cohesion forces. In addition, the increasing pressure exerted by the corrosion products gathered within and/or at the bottom of the coatings defects could contribute to further break adhesion bonds.

Exposure conditions in the HC generated significant color and gloss changes in the waterborne paint coating. Its original ochre coloration became white and lost much of its initial gloss. The color and gloss are associated with the roughness and pigmentation of the paint film; therefore, changes observed mainly in the GSP-WB system (TABLE 8) have been related to the alterations undergone by the film texture and coloration because of the water absorbed over the first 7 days of exposure. After this period, no significant change was observed reason by which the values of these parameters are not shown in the table.

Figure 5 indicates that all the measured E_{corr} values revealed a fluctuating behavior ranging from -0.8 to -0.95 V(SCE), that is, similar but not equal than those obtained in SSC.

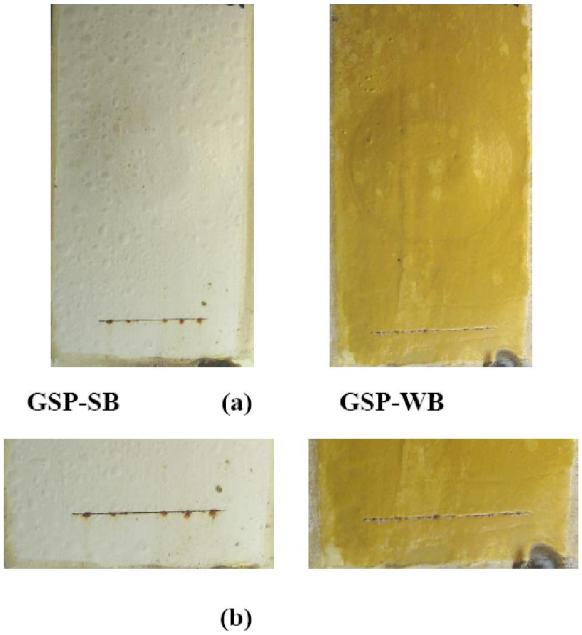


Figure 4 : Final condition of the samples after 42 days exposure in HC. (a) global view and (b) detail of the incision area

Exposed to the HC, and for the first 4 days of testing, both samples exhibited a rapid shift of the E_{corr} values towards more negative values (greater zinc reactivity) indicating premature water and oxygen permeation through the organic film. This process allowed the formation of zinc corrosion products, which could acceptably sealing the coating defects. As a result, the anodic/cathodic areas relationship and, as a consequence, the E_{corr} values of both systems remained relatively stable until finishing the test.

Figure 5 also shows the results of the impedance measurements. The analysis of these data revealed that under these exposure conditions no significant variations occurred in the GSP-SB system, while in the GSP-WB system a gradual deterioration of the protective system was observed.

As in the previous section, both systems showed al least three-time constants under the above mentioned exposure conditions. For both types of samples, the ionic resistance of the organic film remained almost invariant, about 1.10^5 Ωcm^2, throughout the test. This result indicates that under these exposure conditions, the barrier effect afforded by the organic coating is lower than the corresponding to the previous case. This situation is probably due to osmotic reasons because the paint film is more permeable to distilled water vapor than to the salt solution. Taking into account the developed corrosion processes, both systems also showed similar behavior, with a charge transfer resistance of approximately 1.10^8 Ωcm^2 in the initial stages. This value kept constant throughout the exposure period for the GSP-SB system but exhibited a decreasing trend for the GSP-WB system, reaching values of approximately of 1.10^6 Ωcm^2 towards the end of the test.

Exposure in prohesion chamber

To complement the assessment of the behavior of both systems in a less aggressive contaminated atmosphere, the samples were exposed in the Prohesion Chamber for 1100 h. The aging took place in two cycles of 550 h each with the following program: 1 h fog at 25 °C, 0.05% NaCl solution and 0.35% $(NH_4)_2SO_4$, and 1 h drying at 35 °C; pH = 5 and 15 psi pressure.

TABLE 6 : Blistering degree as a function of the exposure time in HC

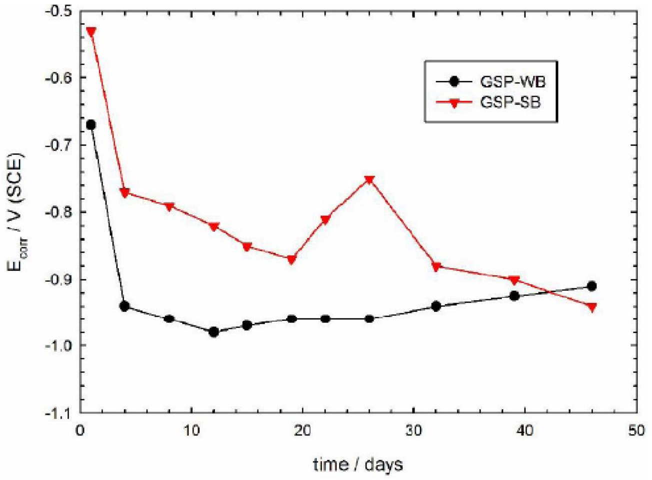
Sample	0d	14d	42d
GSP-SB	10	10	4F
GSP-WB	10	10	6F

TABLE 7 : Adhesion in the intact area before and after exposure in HC

Sample	0d	42d
GSP-SB	5B	2B
GSP-WB	5B	1B

TABLE 8 : Color and gloss evaluation as a function of the exposure time in HC

Sample	Exposure time											
	0d				1d				7d			
	L	a	b	G	L	a	b	G	L	a	b	G
GSP-SB	97.1	0.6	2.5	28.0	96.9	0.6	3.3	30.0	96.7	0.5	3.5	30.9
GSP-WB	59.2	16.3	46.6	76.9	62.5	15.9	42.5	46.9	68.6	14.6	44.3	9.4



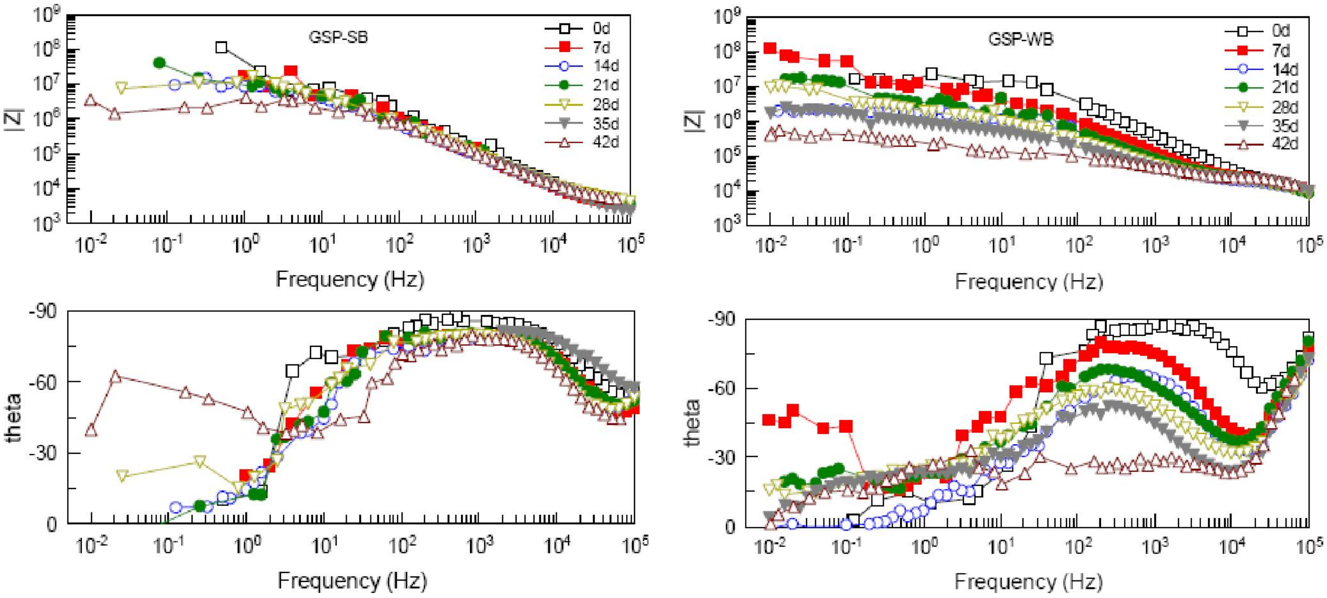
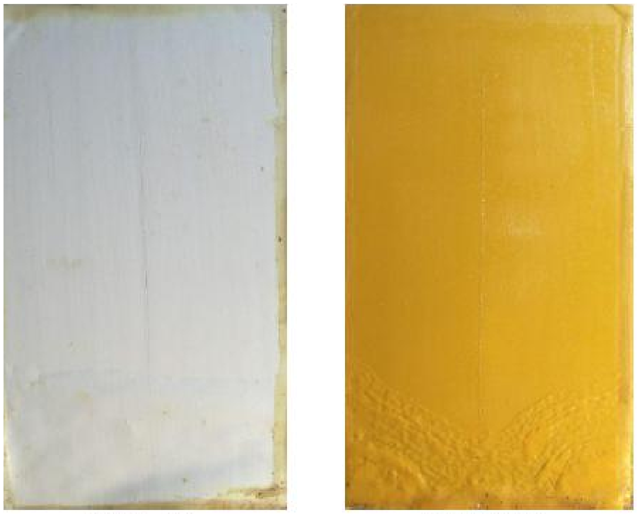


Figure 5 : Evolution of |Z| and (theta) as a function of the exposure time in HC



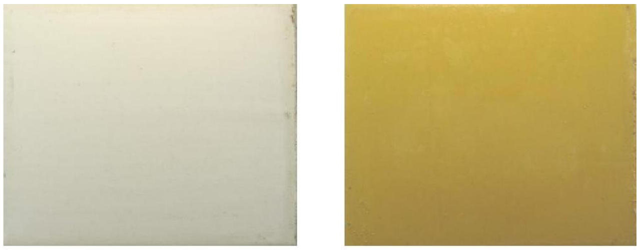
GSP-SB **GSP-WB**

Figure 6 : Final condition of the samples after 1100 h exposure in the PC

Figure 6 shows the samples condition at the end of the test. As seen, the organic coatings did not exhibit any significant deterioration nor the occurrence of corrosion signals and/or adhesion loss in the area of the incision done in the middle zone of the sample. No variations in the paints color and/or gloss were detected.

Exposure to the accelerated weathering test

In order to assess the effect of the UV radiation, replicates of the samples were subjected to the accelerated weathering test for 550 h; the used cycle was 102 min of Xenon light at 63 °C, 18 min of Xenon light and water spray at room temperature. Earlier studies conducted at CIDEPINT reported that the exposure time considered in this work was equal to approximately 20 months of exposure in the urban-industrial



GSP-SB GSP-WB

Figure 7 : Final condition of the samples after 550 h exposure in WC

atmosphere of La Plata city.

Figure 7 shows the samples final condition. As mentioned in the previous section, no significant deterioration of the organic films, occurrence of corrosion signals and/or adhesion loss, and/or changes of color or gloss were perceived.

CONCLUSIONS

Results derived from the comparative study allowed to conclude that the corrosion protection afforded by both painting systems applied on pretreated galvanized steel sheets was satisfactory. However, in the GSP-SB and GSP-WB systems the zinc/paint adhesion strongly depended on the environmental conditions to which the systems were exposed. Thus, the worst behavior was observed in the controlled humidity and temperature chamber, followed by the salt spray chamber, while the samples exposed in the Prohesion or weathering chambers showed optimum performance.

The global analysis of the experimental results coming from the rest of the standardized physicochemical tests allowed to infer that the nanoparticulate pretreatment based on Cr^{+3} and Zirconium used under certain exposure conditions may act as inhibitor of the zinc corrosion and also as a good adhesion promoter for solvent-based or waterborne paints. Consequently, in these cases it could be considered as a valid alternative to replace the Cr^{+6}-based conversion treatment.

ACKNOWLEDGEMENTS

The authors thank to the CAPES/MINCyT (Project 158/09 of Brazil and BR/08/04 of Argentina), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), and the La Plata University of Argentina for the financial support of this research.

REFERENCES

[1] ECCA TC 11 Project Team, Chromium (VI) used in the coil coating industry/Situation regarding health, Safety And Environmental Aspects, Chrome Coverage, **(2004)**.

[2] EPA Federal Register, National emission standards for hazardous air pollutants for source categories: Aerospace manufacturing and rework facilities, September, **60(170)**, 45947 **(1995)**.

[3] Directive number 2003/53/EC of the european parliament and council, 18 June, **(2003)**.

[4] Directive number 2011/65/EU (RoHS2), of the european parliament and council, Restriction of Hazardous Substances, July, **(2011)**.

[5] WTO, World trade organization committee on trade on environment market access impact of ecolabeling requirements, Belgian, **(1998)**.

[6] S.Palraj, M.Selvaraj, P.Jayakrishnan; "Effect of phosphate coatings on the performance of epoxy polyamide red oxide primer on galvanized steel", Prog.Org.Coat., http://www.sciencedirect.com/science/journal/03009440, **54**, 5-9 **(2005)**.

[7] M.R.Yuan, J.T.Lu, G.Kong, C.-s.Che; "Self healing ability of silicate conversion coatings on hot dip galvanized steels"; Surf.Coat.Technol., www.journals.elsevier.com/surface-and-coatings-technology/, **205**, 4507-4513 **(2011)**.

[8] L.Jiang, M.Wolpers, P.Volovitch, L.Ogle; "An atomic emission spectroelectrochemical study of passive film formation and dissolution on galvanized steel treated with silicate conversion coatings", Surf.Coat.Technol., www.journals.elsevier.com/surface-and-coatings-technology/, **206**, 3151-3157 **(2012)**.

[9] G.Von Katen; "JS-2000 auslaugund versiegelungsprozeß ein korrosionsschutzsystem für verbindungselemente", Galvanotechnik, http://www.leuze-verlag.de/en/fachzeitschriften/galvanotechnik, **90(3)**, 650-653 **(1999)**.

[10] T.Bellezze, G.Roventi, R.Fratessi; "Electrochemical study of the corrosion resistance of CrIII-based conversion layer on zinc coatings", Surf.Coat.Technol., www.journals.elsevier.com/surface-and-coatings-technology/, **155(2-3)**, 221-230 **(2002)**

[11] X.Zhang, C.Van Den Bos, W.G.Sloof, H.Terryn., A.Hovestad., J.H.W.de Wit; "Investigation of Cr(III)-based conversion coatings on electrogalvanized steel", Surf.Eng., http://www.springer.com/engineering/production+engineering/journal/11987, **20**, 244-250 **(2004)**.

[12] X.Zhang., C.Van den Bos., W.G.Sloof., A.Hovestad, A.Terryn, J.H.W.de Wit; "The comparison of the morphology and corrosion performance of Cr(VI)- and Cr(III)-based conversion coatings on zinc", Surf.Coat.Technol., www.journals.elsevier.com/surface-and-coatings-technology/, **199(1)**, 92-104 **(2005)**.

[13] B.Da Fonte Jr., M.C.Mich; US Patent, 4.359.345 **(1982)**.

[14] C.R.Tomachuk, C.I.Elsner, A.R.Di Sarli; "Corrosion resistance of Cr(III) conversion treatments applied on electrogalvanized steel and subjected to chloride containing media", Mat.Chem.Phys., http://www.journals.elsevier.com/materials-chemistry-and-physics/, **119(1-2)**, 19-29 **(2010)**.

[15] C.R.Tomachuk, C.I.Elsner, A.R.Di Sarli; "Morphology and corrosion resistance of Cr(III)-based conversion treatments applied on electrogalvanized steel", J.Coat.Technol.Res., http://www.springer.com/materials/surfaces+interfaces/journal/11998, **7(4)**, 493-502 **(2010)**.

[16] L.Li, G.P.Swain, A.Howell, D.Woodbury, G.M.Swain; "The formation, structure, electrochemical properties and stability of trivalent chrome process (TCP) Coatings on AA2024", J.Electrochem.Soc., http://jes.ecsdl.org/, **158**, C274-C283 **(2011)**.

[17] J.N.Yoganandan Balaraju, V.K.William Grips; "The surface and electrochemical analysis of permanganate based conversion coating on alclad and unclad 2024 alloy", Appl.Surf.Sci., http://www.journals.elsevier.com/applied-surface-science/, **258**, 8880-8888 **(2012)**.

[18] S.Ranganatha, T.V.Venkatesha, K.Vathsala; "Electroless Ni–W–P Coating and Its Nano-WS2 Composite: Preparation and Properties", Ind.Eng.Chem.Res., http://pubs.acs.org/journal/iecred, **51**, 7932-7940 **(2012)**.

[19] J.Troiano, D.S.Jordan, C.Hull, F.M.Geiger; "Interaction of Cr(III) and Cr(VI) with hematite studied by second harmonic generation", The J.Phys.Chem.C., http://pubs.acs.org/journal/jpccck, **117**, 5164–5171 **(2013)**

[20] B.A.Boukamp; "Equivalent circuit", Report CT88/265/128, CT89/214/128, University of twente, The Netherlands, **(1989)**.

[21] W.Schwenk; Corrosion control by organic coatings, Jr.H.Leidheiser, Ed., NACE, Houston, TX, 103 **(1981)**.

[22] L.Fedrizzi, L.Ciaghi, B.L.Bonora, R.Fratessi, G.Roventi; "Corrosion behavior of electrogalvanized steel in sodium chloride and ammonium sulphate solutions, A study by E.I.S.", J.Appl.Electrochem., http://link.springer.com/journal/10800, **22(3)**, 247–254 **(1992)**.

[23] C.M.Abreu, M.Izquierdo, M.Keddam, X.R.Nóvoa, H.Takenouti; "Application of electrochemical impedance spectroscopy to study the degradation of polymer-coated metals", Electrochim.Acta, http://www.journals.elsevier.com/electrochimica-acta/, **41(15)**, 2405-2415 **(1996)**.

[24] B.Del Amo, L.Véleva, A.R.Di Sarli, C.I.Elsner; "Performance of coated steel systems exposed to different media: Part I.Painted galvanized steel", Prog.Org.Coat., http://www.sciencedirect.com/science/journal/03009440, **50(3)**, 179-192 **(2004)**.

[25] E.P.M.van Westing, G.M.Ferrari, F.M.Geenen, J.H.W.De Wit; "In situ determination of the loss of adhesion of barrier epoxy coatings using electrochemical impedance spectroscopy", Prog.Org.Coat., http://www.sciencedirect.com/science/journal/03009440, **23(1)**, 89-103 **(1993)**.