Deposition and Characterization of a New Mixed Organic/Inorganic Cerium Containing Coating for the Corrosion Protection of Eletrogalvanized Steel

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Protective coatings have been deposited on electrogalvanized steel by immersion in solutions containing 2-Butyne-1.4-diol propoxylate ($C_7H_{11}O_3$), cerium nitrate, sodium nitrate and sodium sulphate for different immersion periods. The surface morphology and chemical composition of the coatings formed on the electrogalvanized steel were studied using field emission gun scanning electron microscopy, X-ray photoelectron spectroscopy and Fourier Transform Infrared Spectroscopy. The corrosion resistance of the electrogalvanized steel prior to and after surface treatment was investigated by electrochemical impedance spectroscopy in 0.1 mol L^{-1} NaCl solution. The results were compared to the performance of a chromate conversion coating in the same solution. The coatings formed on the electrogalvanized steel surface showed the presence of a mixed organic/inorganic layer containing Ce_2O_3 and CeO_2 which improved the corrosion resistance of the substrate and showed a superior corrosion resistance to that provided by a chromate conversion coating.

1. INTRODUCTION

Conversion coatings with hexavalent chromium are one of the most effective treatments for passivation of electrogalvanized zinc surfaces used in the automotive industry [1,2]. However, since this process generates toxic residues and hexavalent chromium is known to cause oxidation of tissue cells and carcinoma, it has been increasingly eradicated from use. Consequently, there is a need to find a suitable replacement for chromate conversion coatings [3]. Researchers have examined conversion and passivation treatments involving various metal species, including trivalent chromium,

molybdenum, tungsten, vanadium, manganese, ruthenium, niobium and cerium [4-6].

However, to the authors' knowledge, there has been no work undertaken on the development of surface treatments which combine organic and inorganic pre-cursors. In this study, electrogalvanized steel has been immersed in solutions containing 2-Butyne-1.4-diol propoxylate ($C_7H_{11}O_3$), cerium nitrate, sodium nitrate and sodium sulfate for different time periods. The chemical composition and surface morphology of organic based coatings formed have been characterized by various microscopic and spectroscopic techniques and their effect on the corrosion resistance of the substrate was evaluated and compared with that of the same type of material after a standard chromate conversion treatment.

2. EXPERIMENTAL

2.1. Sample preparation

SAE 1010 carbon steel plates with dimensions of 65 mm x 100 mm x 1 mm were used in this study as substrates for zinc electrodeposition. The SAE 1010 steel composition is given in Table 1. Zinc electrodeposition was carried out by immersion in an alkaline bath without cyanide ions using a commercial process. After electrogalvanization, the thickness of the zinc coating obtained was measured using a VEECO/UPA Technology Division X-Ray Fluorescence System model XRF-300 AT, calibrated with the corresponding standard [7]. The electrodeposited zinc layer thickness obtained was (10.0 ± 0.2) μm. The electrogalvanized steel samples were then surface treated. Aqueous solutions containing 2-Butyne-1.4-diol propoxylate (5% v/v), 20mM sodium nitrate, 20 mM sodium sulfate and 50mM hexahydrated cerium nitrate were prepared. The zinc coated surfaces were immersed in the solutions for varying time periods of 1, 10, 20 and 30 minutes, to study how the immersion time affects coating formation and corrosion resistance. The treatment solution pH was 4.7 and the temperature 35 (± 2) °C. The electrogalvanized steel was also coated using a commercial chromating solution for comparison. The chromating treatment involved immersing the samples in a solution with 200 mg.L^{-1} of chromium trioxide at (35 ± 2) °C. This treatment will subsequently be referred in this work as the chromate conversion coating (CCC). After immersion in the treatment solutions, the samples were immediately dried for 15 minutes at 80 ^{0}C and cooled to room temperature.

Table 1. X-ray fluorescence analysis (mass %) of the SAE 1010 carbon steel used as substrate for zinc electrodeposition.

C	Si	Mn	P	S	Cr	Ni	Mo
0.118	0.023	0.310	0.020	0.016	0.024	0.028	0.002

Salt spray tests were carried out as methodology for selecting surface treatments to study in more detail. The salt spray test results eliminated the 30 minute treatment from further study.

2.2. Chemical and morphological characterization

The coatings deposited on the electrogalvanized samples were examined using field emission gun scanning electron microscopy (FEG-SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The FEG-SEM employed was an FEI Quanta 650 FEG High Resolution E-SEM operated at 10 keV. XRD was performed directly on the surfaces using a Rigaku D/MAX II diffractometer operating at 45 kV and 20 mA with a curved graphite crystal monochomator and a broad focus copper source. The samples were scanned at a scan rate of 5 min^{-1} between 10° and 50°. XPS analyses were performed on a Thermo Fisher Scientific Instruments Theta Probe spectrometer. XPS spectra were acquired using a monochromated Al Kα X-ray source (h_v = 1486.6 eV). An X-ray spot of approximately 400 μm radius was employed. Survey spectra were acquired at pass energy of 300 eV and high resolution C 1s and O 1s core level spectra were acquired at a pass energy of 50 eV. Sample specimens were held in place on the instrument sample stage by sprung Cu/Be clips. Quantitative surface chemical analyses were calculated from the high resolution core level spectra following the removal of a non-linear Shirley background. The Thermo Fisher Avantage software was used which incorporates the appropriate sensitivity factors and corrects for the electron energy analyzer transmission function. The XPS spectra were charge shifted with reference to the C1s peak at 285.0 eV to correct for any charging effects during acquisition.

FT-IR was performed using a Perkin Elmer FTIR 16PC infrared spectrophotometer and spectra recorded over a wavenumber range of 4000 to 400 cm^{-1}. An electrogalvanized steel substrate was used without passivation treatment as a reference for comparison with the surface treated samples.

2.3. Corrosion resistance characterization

2.3.1 Salt spray test

The surface treated samples tested in salt spray chamber according to ASTM B-117 standard [8]. The formation of corrosion products on the electrogalvanized steel surfaces was monitored by observation and the development of corrosion was graded using the following criteria: (i) time to white rust appearance; (ii) time to red rust and (iii) time to red rust occupying 10% of the exposed area.

2.3.2. Electrochemical characterization

A standard three-electrode electrochemical cell was used for the electrochemical tests. An Ag/AgCl reference electrode was employed and platinum wire used as the counter electrode. The electrolyte was a 0.1 mol.L^{-1} NaCl solution. The corrosion resistance of the electrogalvanized samples after surface treatment was evaluated by electrochemical impedance spectroscopy (EIS) at the open circuit potential (OCP) as a function of immersion time (1 to 7 days). All EIS measurements were performed in the potentiostatic mode at the OCP. The EIS tests were carried out in the frequency range from 10 kHz to 10 mHz, with a 10 mV amplitude perturbation signal, using a scan rate of 10 points per decade. An area of 1 cm^2 was exposed to the electrolyte.

3. RESULTS AND DISCUSSION

3.1. Surface morphology

Figure 1 shows the morphology of the electrogalvanized steel surfaces in the following conditions: (a) without passivation treatment; (b) passivated with the CCC treatment; (c) passivated by a 1 minute immersion in the test solution (**T1**); (d) passivated by a 10 minutes in the test solution (**T10**); (e) passivated by a 20 minutes immersion in the test solution (**T20**).
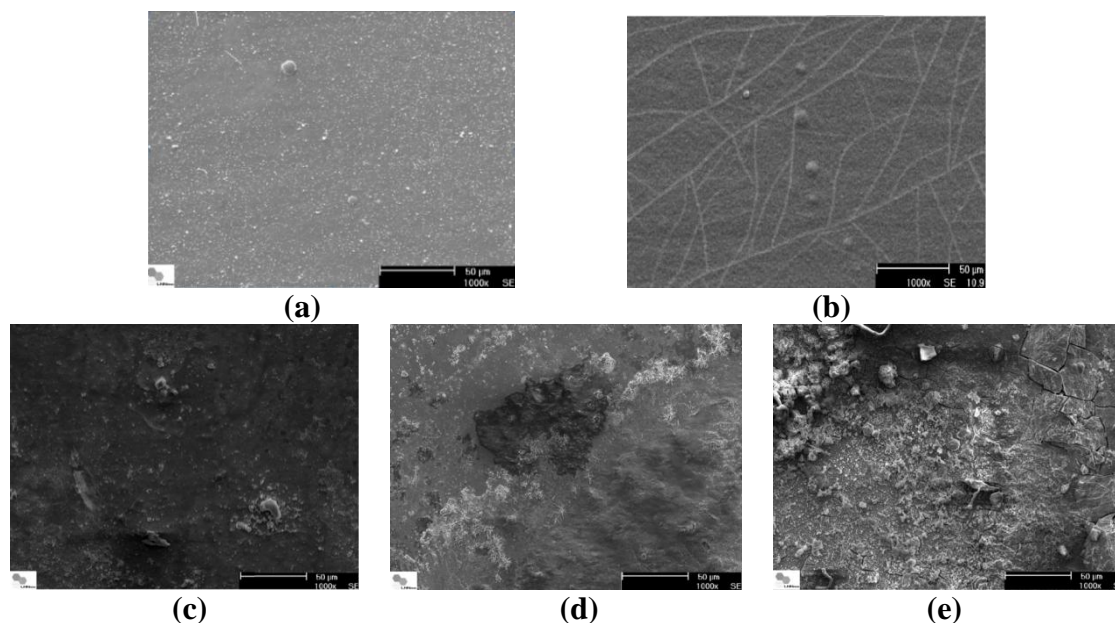

(a)   **(b)**

(c)   **(d)**   **(e)**

Figure 1. FEG-SEM micrographs of the electrogalvanized steel surface: (a) untreated; (b) after chromate conversion coating (CCC) treatment; (c) after 1 minute immersion in the test solution (**T1**); (d) after 10 minutes immersion in the test solution (**T10**); (e) after 20 minutes immersion in the test solution (**T20**).

The surface of the electrodeposited zinc coating (Figure 1a) is fairly homogeneous but there are areas where thicker deposits (round features) are observed. Similar features can also be seen on the surfaces following CCC treatment. For the CCC treated surface (Figure 1b), cracks in the coating are also observed which are characteristic for this treatment. The morphologies of the coatings obtained following the test surface treatment of 2-butyne-1.4-diol propoxylate + $Ce(NO_3)_3$ + $6H_2O$ $NaNO_3$ + Na_2SO_4 after 1, 10 and 20 minute immersion are shown in Figures 1c, 1d and 1e respectively. Lengthening the time of immersion in the solution leads to an increased surface roughness and inhomogeneity of the surface morphology. Hence, the coating appears to thicken with immersion time and cracks are observed in the coating after longer periods of immersion (20 minutes). The morphological results suggest that the 10 minute immersion (T10) gives rise to the most uniform and protective coating.

Salt spray tests results obtained for the CCC, T1, T10 and T20 treatments are shown in Table 2 (average of five samples). The T10 surface treatment yields a corrosion resistance superior to that

offered by the chromate conversion coating (CCC), indicated by the longer time observed before the appearance of white and/or red corrosion products on the surface.

Table 2. Corrosion performance of the electrogalvanized steel with surface treated samples in salt spray test according to ASTM B117. CCC corresponds to chromating conversion coating treatment and T1, T10 and T20 to surface treatments by immersion in 2-Butyne-1.4-diol propoxylate solution with 0.5 mol.L^{-1} cerium nitrate (pH 4.7) and sodium nitrate and sodium sulfate at $(35 \pm 2)°C$ for 1, 10 and 20 minutes respectively.

Surface condition	Time for rust (h)		
	White rust	First point red rust	10% red rust
Zinc	8	75	80
CCC	96	240	250
T1	90	180	206
T10	120	336	400
T20	120	206	230

3.2. Chemical characterization

3.2.1. FTIR

It was important to determine if an organic film had been formed on the surface of the electrogalvanized steel by immersion of the samples in 2-butyne-1.4-diol propoxylate + $Ce(NO_3)_3$ + $6H_2O$ $NaNO_3$ + Na_2SO_4 test solution. FT-IR spectra recorded for the samples exposed to the T1, T10 and T20 treatments are shown in Figure 2.
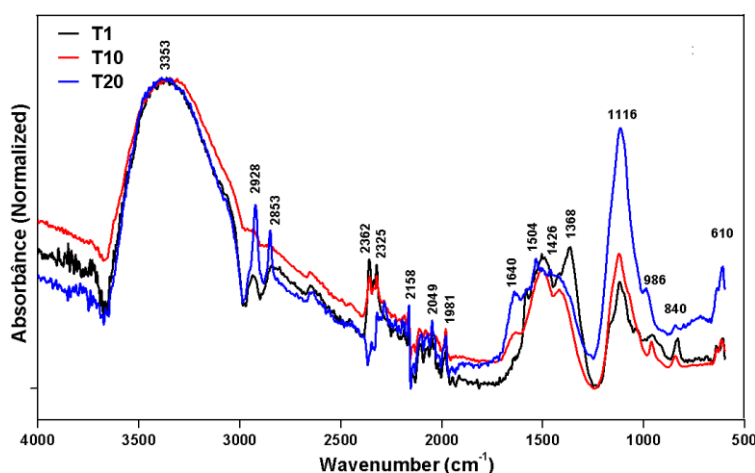

Figure 2. Normalized FT-IR spectra of electrogalvanized steel surfaces after surface treatments corresponding to 1 minute immersion in the test solution **(T1)**; 10 minutes immersion in the test solution **(T10)**; 20 minutes immersion in the test solution **(T20)** composed of 2-butyne-1.4-diol propoxylate + $Ce(NO_3)_3$ + $6H_2O$ $NaNO_3$ + Na_2SO_4 .

Peaks corresponding to C-H groups are seen at wavenumbers of 840 cm^{-1} and 986 cm^{-1} for the surfaces treated in the test solution, independent of immersion time. These correspond to the C-H bond stretch in (CH$_2$-) and out of plane (-CH$_3$) respectively. The (C-O) bond stretch was observed at 1116 cm^{-1}. The peaks at 1116 cm^{-1} and 1368 cm^{-1} show the presence of the carboxyl group [9]. The intensity of the peak at 1116 cm^{-1} increases with treatment time due to thickening of the organic coating. The absorption band centered between 1655-1630 cm^{-1} corresponds to C=C stretching. The peaks reported above suggest that parts of the precursor molecule or structures derived from it were incorporated into the surface coating on the Zn surface. The peaks seen at 1426 and 3500 cm^{-1} correspond to inorganic compounds and are most probably associated with ZnCO$_3$, Zn(OH)$_2$ or Zn$_5$(CO$_3$)$_2$(OH)$_6$. The presence of carbonates occur due to the chemical reaction of carbonate ions in the solution and Zn^{2+} ions due to corrosive attack of the substrate [10]. These peaks between 1400 and 1500 cm^{-1} are most probably associated with the presence of Zn(OH)$_2$. The presence of cerium compounds in the coating was confirmed by the small peaks at 610 and 2853 cm^{-1}, associated with the vibrational modes of CeO$_2$ and Ce(NO$_3$)$_3$ respectively [11] for all treatment times. The intensities of these peaks increased with treatment time, indicating that longer immersion times increase the cerium incorporation into the surface coating or the coating is increasing in thickness.

3.2.2. XPS

The chemical composition of the surface coatings was also investigated by XPS. Depth profiles were also recorded, providing information on the depth distribution of elements within the layers formed. The XPS survey spectra corresponding to treatments T1, T10 and T20 are shown in Figure 3.
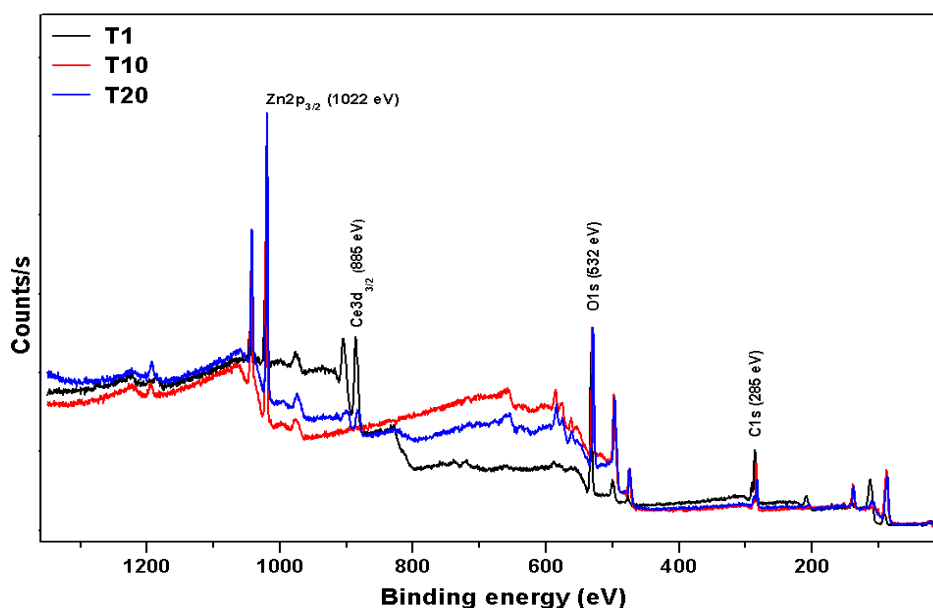

Figure 3. XPS survey spectra of the electrogalvanized steel after surface treatments corresponding to 1 minute immersion in the test solution **(T1)**; 10 minutes immersion in the test solution **(T10)**; 20 minutes immersion in the test solution **(T20)** composed of 2-butyne-1.4-diol propoxylate + Ce(NO$_3$)$_3$ + 6H$_2$O NaNO$_3$ + Na$_2$SO$_4$.

The elements identified from the survey spectra for all the test treatments were carbon, oxygen, zinc and cerium. The narrow scans for Zn 2p, Ce 3d, C 1s and O 1s peaks as a function of sputtering time (etch time) are shown in Figure 4. The samples were analyzed after up to 480 seconds of sputtering. All of the peaks are shifted relative to the C1s binding energy of 285.0 eV (C-C or C-H), with an error of ± 0.2 eV [12].
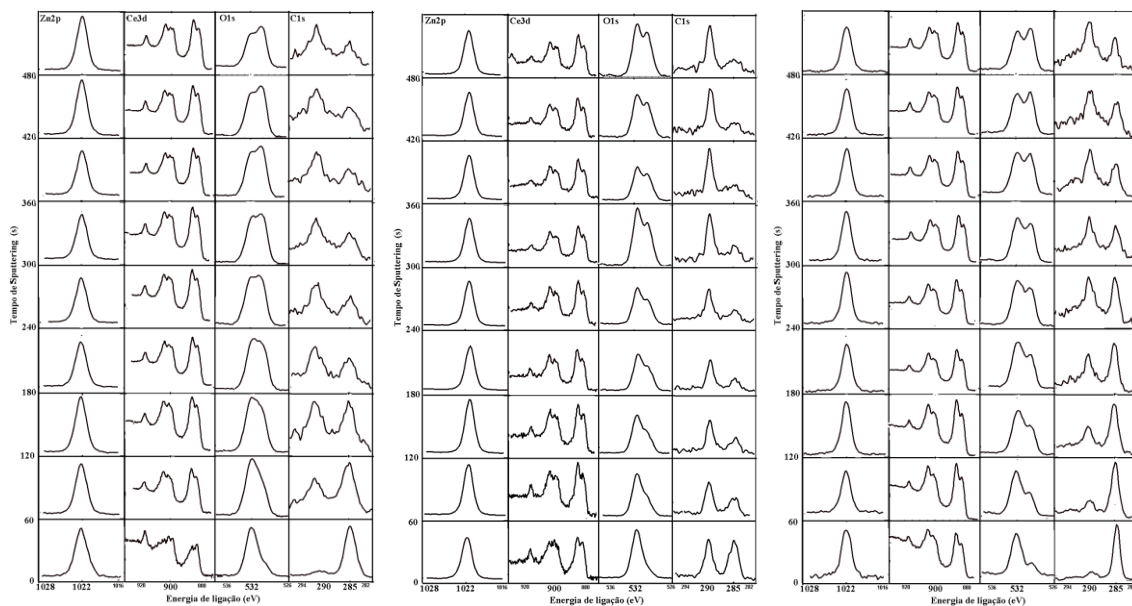

Figure 4. XPS Zn 2p, Ce 3d, O 1s and C 1s spectra as a function of sputtering time (in seconds) for treatments (a) T1 (b) T10 and (c) T20.

The zinc concentrations obtained by XPS as a function of sputtering time show an increase in the metallic Zn concentration with increasing depth for all of the coatings. After 480 seconds of sputtering the concentration of the metallic Zn peak varies substantially with treatment time. As the treatment time increases the metallic Zn concentration after 480s of sputtering decreases, being 32 at.% for T1, 11 at.% for T10 and 1 at.% for T20. This is due to thickening of the coating.

Curve fitting the C 1s peaks for T1 treatment show that carbon is functionalized as C–C/C–H (binding energy = 285.0 eV), C–O/C–OH, (binding energy = 286.3 – 286.4 eV), C=O (binding energy = 287.8 – 287.9 eV) and O–C=O (binding energy = 288.8 – 289.5 eV). Table 9: Atomic Concentrations of oxides of cerium (III and IV) obtained from the peak adjustments Ce 3d5/2 as a function of sputtering time, T1.

The adjustments to the peak of carbon references T1 immersion treatment (1 minute in a solution of cerium nitrate hexahydrate, sodium nitrate, sodium sulfate and second butyne 1,4 diol propoxylate) showed that functionalized carbon as CO, C-OH , C = O and OC = O represent the largest portion of the relative concentration. The carboxyl group associated to connections with the metal substrate, bidentate ligand increases with sputtering time of confirming the presence of this group more internally in the conversion layer, *i.e*. on the substrate zinc oxide / hydroxide / metal.

For all of the treatment times, the intensity of the carboxyl group increases with sputter time, indicating C=O species are present within the film bulk. The XPS results support the FT-IR results indicating that the treatments have led to the formation of an organic film on the zinc substrate. The decrease of the 285.0 eV peak as a function of sputtering time is due to the high concentration of adsorbed hydrocarbon contamination at the surface. The increase of the 290 eV peak, characteristic of organic compounds, carbonates with sputtering time, indicates the presence of organic species in the coating.

Curve fitting of the Zn $2p_{3/2}$ peak allows the zinc metal and zinc oxide peaks to be identified, based on peak full width half maximum (FWHM) [13]. For the T1 treatment, zinc is mainly found as oxide at the surface (no sputtering). The T1 treatment (corresponding to 1 minute of immersion in the acid solution (pH 4.2)) resulted in corrosive attack of zinc, leading to the formation of zinc hydroxide/oxide. Examining the O 1s peak, it is clear that two O 1s components are present for all of the treatments and at all sputter times and the lower binding energy component tends to increase with sputtering time. The lower binding energy peak at around 530 eV most probably corresponds to metal oxide (e.g. zinc oxide/cerium oxide) and the peak at higher energy (around 532 eV) could correspond to a number of components; zinc hydroxide, zinc carbonate or carboxylic acid groups [14].

XPS results for treatments T1, T10 and T20 show cerium in two oxidation states. The XPS spectrum for cerium oxide is complex, including various satellites peaks, often labeled as **v⁰**; **v'**; **u⁰**. **u'**. **v. v''**; **v'''**; **u**; **u''** and **u'''** [15,16]. The peaks observed in the Ce 3d spectra for all surface treatments show the presence of both Ce^{3+} and Ce^{4+}, indicating that Ce is present in the coating as Ce_2O_3 and CeO_2 [16,17]. The presence of these species is expected improve the corrosion resistance of the coating on the zinc surface.

It is clear that he coating formed after 20 minute immersion is thicker, however. the FEG-SEM results suggest that the coating is inhomogeneous and cracked, hence is not forming a continuous film and therefore might not provide effective protection against corrosion. The XPS and FT-IR results have shown the presence of carbonyl groups, indicating that the test treatments form a mixed inorganic/organic film which is bound to the zinc substrate. The carbon concentrations for carbon bonded as carboxyl corresponding to increasing periods of treatment accounted for 4 at.%. 35 at.% and 30 at.% for T1, T10 and T20 respectively. These results suggest that 1 minute of immersion was insufficient to form significant amounts of carbonyl groups and that 10 minutes is ideal time for formation of a tightly linked organic layer.

All of the treatments show the presence of Ce_2O_3 and CeO_2 at the surface. The oxidation of cerium from trivalent to the tetravalent state offers protection to the substrate because the tetravalent ions have lower solubility. Consequently, higher comparative concentrations of Ce tetravalent to trivalent are beneficial for the protection of substrate, when cerium is present at defective sites in the coating.

3.2.3. Electrochemical characterization

The corrosion resistance of the electrogalvanized steel following the various test treatments was evaluated in 0.1 mol L^{-1} NaCl solution and compared to that of the CCC coated and untreated

electrogalvanized steel surface. The electrochemical behaviour for the different surfaces tested over increasing time periods (1-7 days) is presented as Nyquist diagrams in Figure 5.
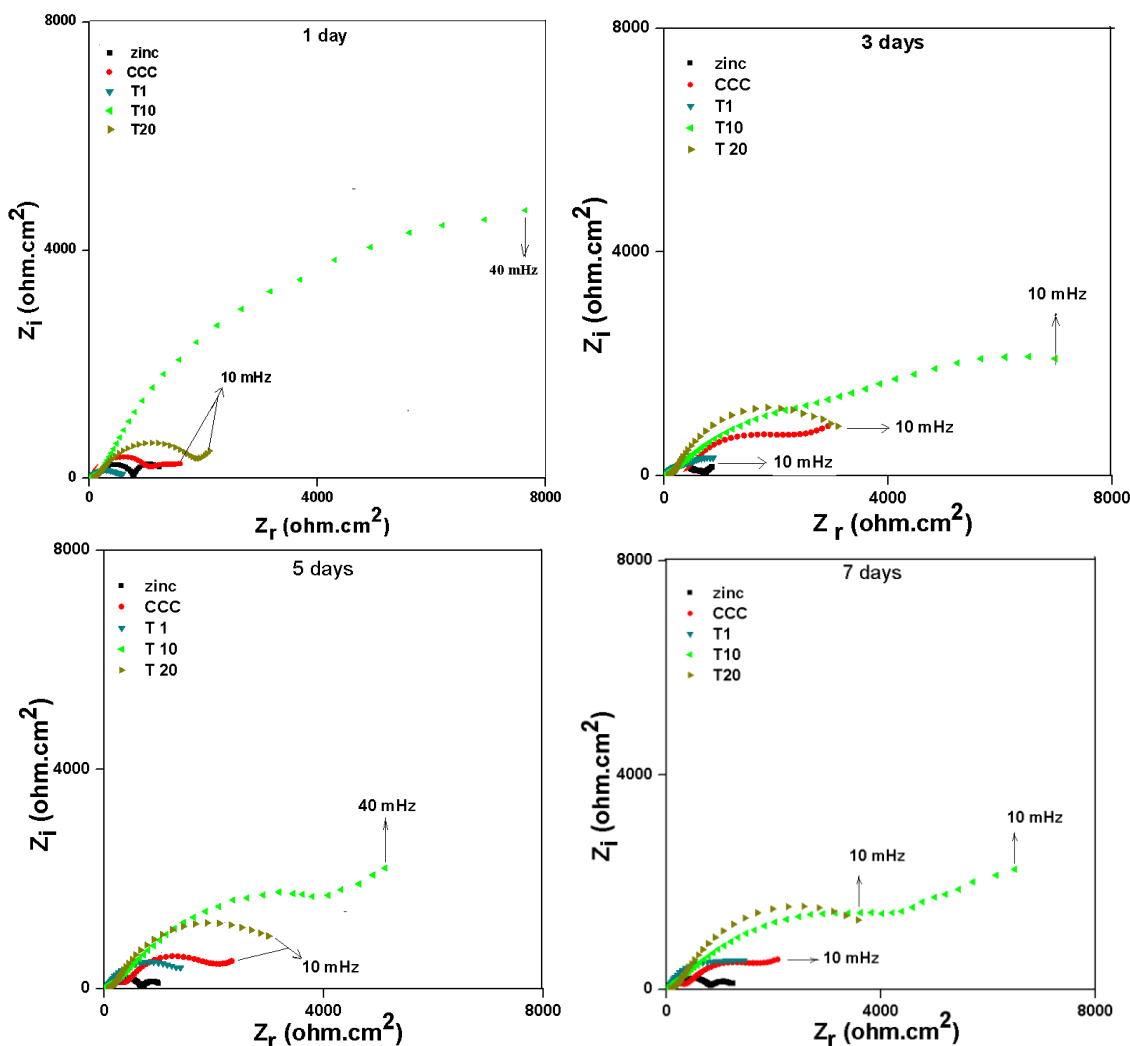

Figure 5. Nyquist diagrams of the various surfaces tested for periods corresponding to 1, 3, 5 and 7 days of immersion in 0.1 mol L^{-1} NaCl solution.

The results in Figure 5 show much higher impedances for the T10 treatment after one day exposed to the NaCl solution compared to the other surfaces tested. However, a large decrease in the impedance was seen between one and three days of exposure indicating a rapid penetration of the electrolyte through the coating to the surface. In addition, between three and five days of exposure, there is indication of diffusion controlled corrosion processes occurring at low frequencies. This type of diffusion control was not seen associated to the T1 or T20 treatments for any of the exposure periods. Furthermore, for the whole exposure period, the impedances associated with the T10 treatment were superior to that of the CCC surface.

In spite of the lower impedances of the CCC surface compared to the T10 treatment, both showed similar shapes in the plot, with the presence of a small arc at high frequencies, followed by
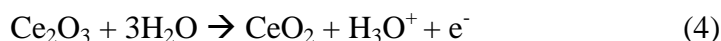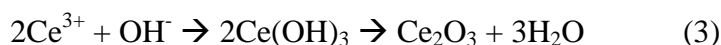
larger arc at medium frequencies and a diffusion controlled process at lower frequencies. The results suggest that similar chemical processes are occurring on both surfaces.

The mechanism proposed in the literature for the protection of the metallic substrates by chromate conversion coatings is composed, according to Zhang [1] by the following reactions:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2 \qquad (1)$$

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \qquad (2)$$
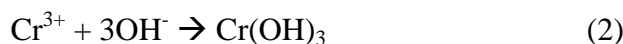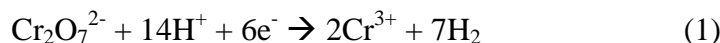
These reactions lead to precipitation of corrosion products on the exposed metallic substrate slowing down the charge transfer processes due to hindering of the access of the corrosive species to the substrate that favors diffusional controlled processes as it was indicated in the electrochemical impedance data at the low frequencies.

Similarly to the corrosion protection chromate conversion coating, it is proposed that the cerium ions incorporated in the coating formed by the new organic/inorganic cerium containing coating, promotes the following reactions occurring at the zinc surface [19]

$$2Ce^{3+} + OH^- \rightarrow 2Ce(OH)_3 \rightarrow Ce_2O_3 + 3H_2O \qquad (3)$$

$$Ce_2O_3 + 3H_2O \rightarrow CeO_2 + H_3O^+ + e^- \qquad (4)$$

leading to precipitation of insoluble products that also hinder the access of corrosion species to the metallic substrate favoring diffusion controlled processes.

In order to investigate changes occurring at the surface with the treatment for the best performing treatment (T10), EIS data was recorded daily over a seven day period and the results are presented in Figure 6 as Nyquist and Bode phase diagrams. The results show that after the impedance decrease between one and three days of exposure, the impedance remained fairly stable until the end of the test (7 days).

It is proposed that the large impedance decrease seen between one and three days of exposure corresponds to the electrolyte easily permeating through the coating to the zinc substrate, promoting corrosive attack. The fast attack of the substrate leads to the formation of zinc corrosion products of low solubility (insoluble) that precipitate on the surface hindering the diffusion of corrosive species into the metallic substrate or of the corrosion products away from the substrate by partial blockage of defects in the coating. This is supported by stabilization of the impedance from 5 days of immersion with the clear indication of diffusional processes at the low frequency range. This stabilization was

The experimental data shown in Figure 6 was fitted to the electrical equivalent circuit (EEC) proposed and illustrated in Figure 7. The EEC component values were estimated using Zview software and the results obtained are presented in Table 3.
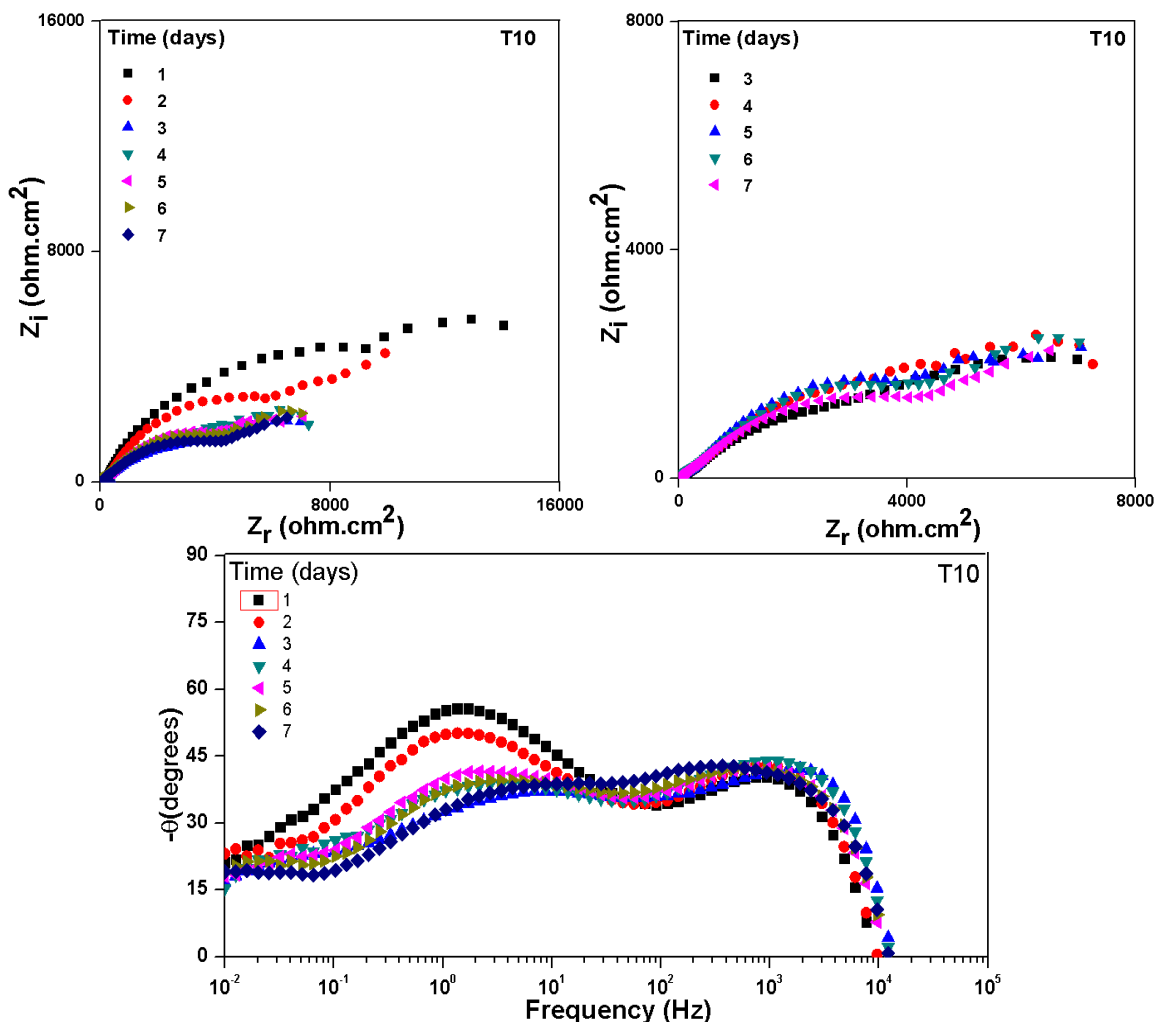
Figure 6. Nyquist and Bode phase angle diagrams for the electrogalvanized steel with treatment T10 for 7 days of immersion in 0.1 mol L^{-1} NaCl solution.
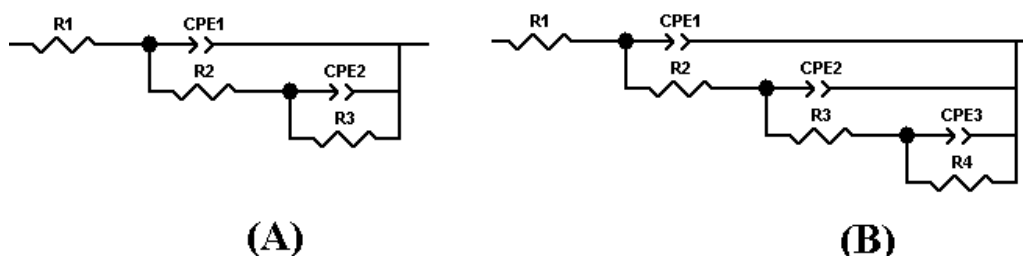

Figure 7. Equivalent circuits used for fitting the EIS experimental data corresponding to (A) 1 day and (B) 2 to 7 days of immersion in aerated 0.1 mol L^{-1} NaCl solution.

The CPE$_1$ values which are in the range from 2 to 30 μF cm^{-2} suggest that these are related to charge transfer processes at the interface substrate electrolyte exposed underneath the defects and porosities in the organic layer formed on the surface by the surface treatment tested.

The fairly low R$_1$ values (in the range from 145 to 445 Ω cm^2, *i.e.* order of hundreds of Ω cm^2, suggest a defective film formed on the surface and this is supported by the surface observation.

Nevertheless, the resistance increases with time of exposure most probably due to the increasing blockage of the coating porosities/defects by corrosion products. This is also supported by the fast decrease in the resistance associated with the corrosion products formed at the film defects (R_2) and accompanied by the rapid increase in the CPE_2 values. The CPE_2 evolution with time suggests the accumulation of porous corrosion products on the zinc substrate exposed at the defective areas of the coating, mainly for periods above 5 days of immersion. This might hinders the diffusion of corrosion products from the metallic substrate outwards, and it was supported by the increasing diffusion contribution suggested by the results. This type of mechanism has been proposed in literature for the corrosion of zinc [18].

The low frequency processes can be attributed to corrosion of the substrate in a diffusion controlled process, which occurred over the whole period of the test and is associated to the CPE_3-R_3 couple related to the low frequency data. The associated resistance steadily decreases with time and decreases to less than half of its original value between 4 and 5 days of immersion. This could be caused by the harsher conditions typical of crevice generated beneath the porous corrosion products accumulated at the defective areas of the organic coating. Despite of this, the comparison between the results related to the CCC treatment and that of the T10 treatment, shows that this last one leads to better corrosion protection of the substrate during the whole period and a fair stabilization of the electrochemical properties of corrosion from 5 days onwards. It is proposed that this stabilization occurs due to the anchoring of the corrosion products by the coating containing cerium in its structure.

The presence of anchoring sites in the organic film keeps the corrosion products attached to the surface, delaying the failure of the coating layer, and prolonging the corrosion protection compared to the other coatings tested. According to the literature [19], cerium conversion layers have been largely studied for the corrosion protection of steel or galvanized substrates and the presence of these coatings increases the impedance of the coated surface. Thus, in the present study it is also proposed that Ce_2O_3 and CeO_2 incorporated in the coating provides further protection to the substrate, mainly at the defective sites in the coating.

Table 3. EEC components values according to the model proposed in Figure 7.

Circuit Elements	Exposure time (days)	1	2	3	4	5	6	7
Rs (Ω)		28.54	28.1	27.85	28.64	27.37	31.72	32.58
CPE_1 $\mu Fcm^{-2} s^{(\alpha-1)}$		1.89	2.71	4.68	4.80	10.1	17.5	30.2
α		0.94	0.89	0.87	0.88	0.85	0.80	0.82
R_1 (Ω cm^2)		144.5	228	215	200	257	302	445
CPE_2 $\mu Fcm^{-2} s^{(\alpha-1)}$		1.90	4.50	13.2	42	98	107	174
α		0.89	0.84	0.87	0.72	0.72	0.65	0.43
R_2 (Ω cm^2)		17260	15000	8823	7912	7329	6791	6084
CPE_3 $\mu Fcm^{-2} s^{(\alpha-1)}$			126	241	273	281	325	805
α			0.47	0.39	0.48	0.41	0.53	0.51
R_3 (Ω cm^2)			15105	12590	12000	4734	3290	2648

4. CONCLUSIONS

The treatment proposed in this study for corrosion protection of electrogalvanized steel consisted in the immersion of the samples in a complex solution composed of a mixture of 2-butyne-1.4-diol propoxylate with cerium nitrate, sodium sulfate and sodium nitrate resulted in the formation of a mixed polymeric/inorganic film on the surface. The film formed showed the incorporation of Ce as Ce_2O_3 and CeO_2. The treatment time was an important factor affecting the protective properties of the substrate. Among the treatment times tested, a 10 minute treatment time showed the best corrosion performance. Longer periods of immersion increased the number of defects in the coating due to strong attack of the zinc surface in the acidic solution used for surface treatment. The improved corrosion resistance of the samples with the treatment for the selected period of time was indicated by electrochemical and salt spray tests. The comparison of the electrochemical and salt spray test results for the various types of surface treatment tested showed that the passivation treatment in 2-butyne-1.4-diol propoxylate with cerium nitrate, sodium sulfate and sodium nitrate provided better corrosion protection than a chromate conversion coating.

References

1. X. Zhang, C. van den Bos, W.G. Sloof, A. Hovestad, H. Terryn, J.H.W. de Wit, *Surf. Coat. Tech.,* 199 (2005) 92.
2. B. P. Wilson, J. R. Searle, K. Yliniemi , D. A. Worsley, H. N. McMurray, *ECS Trans*., 50 (2013) 53.
3. F.W. Eppensteiner, M.R. Jenkins, *Met. Finish.*, 98 (2000), 497.
4. T. Peng, R. Man, *J. Rare Earths*, 27 (2009)159.
5. L. Xia, E. Akiyama, G. Frankel, R. McCreery, *J. Electroc. Soc*., 147 (2000) 2556.
6. C. R. Tomachuk, C. I. Elsner, A. R. Di Sarli, O. B.bFerraz,. *J. Coat. Techn. Res.*, 7 (2010) 493.
7. R. Klockenkämper, A. Von Bohlen, *Spectroc. Acta Part B*, 44 (1989) 461.
8. V. Subramanian, W. J. Van Ooij, *Surf. Engineer,* 15 (1999) 168.
9. H.Wang, R. Akid, *Corr. Sci.,* 50 (2008) 1142.
10. T. E. Graedel, *J. Electroc. Soc*., 136 (1989) 193C.
11. Y. Hamlaoui, F. Pedraza, C. Remazeilles, S. Cohendoz, C. Rébéré, L. Tifouti and J. Creus, *Mat. Chem. Phys*., 113 (2009) 650.
12. J. E. Castle, *Surf. Interf. Anal*., 33 (2002) 196.
13. C.F. Miller , G.W. Simmons, R.P. Wei, *Scri. Mater.*, 42 (2000) 227.
14. G. Beamsom, A. Bunn, D. Briggs, *Surf. Interf. Anal*., 17 (1991) 105.
15. I. Odnevall, C. Leygraf, *ASTM Spec. Tech. Public.,* 1239 (1995) 215.
16. M. Romeo, K. Bak, J. El Fallah, F. Le Normand, and L. Hilaire, *Surf. Interf. Anal.,* 20 (1993) 508.
17. E. Bêche, P. Charvin, D. Perarnau, S. Abanades,G. Flamant, *Surf. Interf. Anal.*, 40 (2008) 264.
18. A.P. Yadav, A.Nishikata, T. Tsuru, *Corr. Sci.,* 46 (2004) 361.
19. K. Aramaki, *Corr. Sci.,* 43 (2001) 1573.