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Corrosion of painted galvanneal steel

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Abstract

The annealing galvanized steel (Galvanneal) is produced from hot-dip galvanized steel thermally treated. The result is a coating formed by Fe-Zn phases. Its main advantage over the conventional galvanized steel is the absence of the characteristic spangles affecting these coatings and the presence of iron providing better weldability than the pure zinc coating. In this work, the corrosion behavior of pre-treated and painted with environmentally friendly schemes, conventionally hot-dip galvanized, and annealing galvanized (Galvanneal) steel were studied. A γ-mercaptopropyltrimethoxysilane (MTMO) pre-treatment was applied. A waterborne polyurethane paint developed at CIDEPINT was used. Assays were performed in the salt spray and controlled humidity chambers. The metal-paint adhesion was determined by Tape Test. The systems deterioration was evaluated by means of periodical visual inspections, optic and electron microscopes, EDXS, and electrochemical impedance measurements. The MTMO showed to be a good adhesion promoter for the systems exposed to the present testing conditions.

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Keywords: Galvanneal, Galvanized steel, Corrosion, Paint, Duplex system

1. Introduction

In the automotive industry, the increasingly demanding market requirements have made in recent years significantly increase the percentage of coated steel sheet use for manufacturing both bodywork and structural parts of automobiles. In this sense, the electro-galvanized and Galvanneal are the two most commonly used materials [Goodwin et al. (2011), Suzuki (2011)]. The latter is gaining more and more markets due to its low cost and

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excellent weldability conditions. The Galvanneal process involves applying a heat treatment after hot-dip galvanizing in order to eliminate the typical spangles of these coatings, increase the roughness to improve paint adhesion and improve the weldability. During this annealing are formed by diffusion different phases of Fe-Zn, resulting in a coating consisting of inter-metallic layers with decreasing Fe content from the interface coating/substrate to the surface, reaching here values between 9 and 12%.

When galvanized steel is painted, either for being exposed to a very aggressive medium or for aesthetic reasons, is built up the so-called duplex system, which acts synergistically, since the protection provided by the paint plus the zinc coating is greater than the sum of both separate effects. [van Eijnsbergen (1994), Cabanelas et al. (2007), Pérez et al. (2002), del Amo et al. (2004)]. Among the failures that significantly affect the service life of these systems, the most important are related to adhesion problems at the organic coating-zinc interface. In this sense, the surface pre-treatments have been a crucial step to mitigate this type of failure. Nowadays, in Argentina most pre-treatments are based on Cr(VI), however, since these products are harmful to the environment and health, in recent years several studies are being made for it replacement and, in this sense, silane pre-treatments have proven to be one of the most interesting alternatives [van Ooij et al. (2005), Gang et al. (2009), Gang et al. (2010)]. Silanes form a protective film on the zinc substrate by adhering to it by covalent bondings of the type Si-O-Metal formed by the hydrolysis products of R'O groups and the film of oxy-hydroxides present on the metal, greatly improving the paint-substrate adhesion [Chico et al. (2012)].

On the other hand, solvent-based polyurethane paints have excellent weather resistance under various atmospheric conditions like marine environments with high humidity and solar radiation, without damaging its gloss and color [Elsner et al. (2012)]. Nevertheless, volatile organic solvents are polluting and this has led to study alternatives to diminish their concentration or replace them by changing painting formulations, being one alternative the use of water as solvent. Compared with solvent-based paints, the waterborne ones have less resistance to weathering but in recent years were reached formulations whose performance is highly satisfactory.

In this paper, the corrosion behavior of conventional hot-dip galvanized steel and annealing galvanized steel (Galvanneal), both pre-treated and painted with environmentally friendly schemes was studied. γ-mercaptopropyltrimethoxysilane (MTMO) was used as adhesion promoter and a water-based polyurethane paint developed at the CIDEPINT as organic coating. To evaluate the corrosion behavior, samples were exposed in salt spray chamber (SSC) or humidity chamber (HC). Dry and wet paint adhesion were evaluated by the tape and impact tests while the systems degradation was quantified by visual inspection, optical and electron microscopes, EDXS and electrochemical impedance spectroscopy (EIS).

2. Experimental procedure / methodology

Samples (15 x 7.5 x 0.70 cm) of galvanized steel (ZN) and Galvanneal (GAL) were built up from continuous hot-dip galvanized sheets of commercial origin. All the samples were subjected to an electrochemical cleaning by dipping for 20 s in a 10% w/v NaOH solution and applying a current of 9 A. The substrates roughness was measured with a Hommel Tester T1000 profilometer and the results are shown in Table 1, where Ra is the average roughness and Rt the full or maximum roughness. To evaluate the effect of MTMO as adhesion promoter, some samples were pre-treated with silane in the conditions listed in Table 2. With this aim, 3.6 mL of MTMO were mixed with 5.4 mL of a solution 60% v/v methanol and 40% v/v distilled water. The pH of this last solution was adjusted to 4.0 with acetic acid before adding the silane. After 1 h hydrolysis with constant stirring, the obtained solution was diluted with 81.3 mL of the same methanol-distilled water solution. MTMO final concentration was 4% v/v. The samples were immersed in the hydrolyzed MTMO solution for 1 min and vertically cured in an oven at 80 ± 1 ºC for 10 min [Bexell et al. (2007)]. Samples were kept in desiccators until being painted. All the samples were coated with a three-component water-based polyurethane paint developed at the CIDEPINT (Table 3). The thickness of the metal coating was calculated by gravimetry, and the corresponding to the on organic coatings by a magnetic probe, according to ASTM B 499 standard; their values are reported in Table 4. The silane film thickness was measured by SEM.

For a proper paint curing the painted samples were kept in desiccators at 25 °C for 72 h.

After the paint film curing, its adhesion to the substrate before and after accelerated tests was assessed using the Tape Test, ASTM D-3359 standard. Impact tests were performed too, taking the ASTM D2794 standard as reference. To simulate a failure in service, the organic coating of both types of samples were cut up to the substrate and then, by triplicate, exposed the humidity chamber (HC) (ASTM D-2247 standard) and salt spray chamber (SSC)

(ASTM B-117 standard). The evolution of the protective performance was assessed periodically by visual inspection and photographic records complemented by EIS measurements.

Table 1. Surface roughness of the metal coating.

Sample	Ra (μm)	Rt (μm)
GAL	1.26	10.2
ZN	0.44	3.14

Table 2. Conditions for applying the silane used as pre-treatment.

Silane	Concentration % (v/v)	Immersion time (min)	Curing time (min)	Curing temperature (ºC)
MTMO	4	1	10	80

Table 3. Components of the used polyurethane paint.

Paint component	% (p/p)
A - Acrylic base	87.46
B - Converter: isocyanate	8.75
C - Dispersed Pigment: ochre ferrite	3.79

Table 4. Metallic and organic coatings thickness.

Sample	Galvanic film (μm)	Paint film (μm)
ZN	20	112
GAL	11	115

The electrochemical cell was a typical three-electrode one with an acrylic tube placed on the samples leaving exposed to the electrolyte a geometric area of 15.9 cm^2; the tube was maintained on the sample by means of clamps and a rubber O-ring performed the seal. The electrolyte was a naturally aerated 0.5 M NaCl solution, while the auxiliary and reference electrodes were, respectively, a platinum mesh and a Saturated Calomel Electrode (SCE). The impedance spectra were obtained in the potentiostatic mode at the corrosion potential, with a signal amplitude of 15 mV peak to peak and in the frequency range 1.10^{-2} to 1.10^{5} Hz. The impedance module at low frequencies, considered as the total system resistance [Barcelo et al. (1998), Kendig et al. (1999), Almeida et al. (1998), Magalhaes et al. (1998)], was taken as a parameter for the evaluation of the system corrosion behavior.

3. Results and discussion

3.1 Substrates characterization

Fig. 1 shows the surface of the two considered materials without pre-treatment. As seen, the GAL sample looks rougher than the ZN one, which is in accordance to the measured roughness values. Besides, as determined by EDXS, the Fe content in the GAL sample surface was 11%, it was uniformly distributed on the surface and its concentration was coincident with the delta phase ($FeZn_{10}$) [Marder (2000)]. In the case of ZN samples, was detected Zn and small amount of Al, an element added to the zinc bath for preventing the growth of FeZn phases.

The SEM photograph of the ZN sample surface after being pre-treated with MTMO, Fig 2, allows to observe that the silane film was uniformly distributed but with the presence of cracks of about 2 μm wide.

The silane film thickness was about 500 nm (estimated by SEM). By EDXS it was determined that the MTMO film was composed by 41.7% C, 29.7% O, 28.4% Si and 0.2% S.

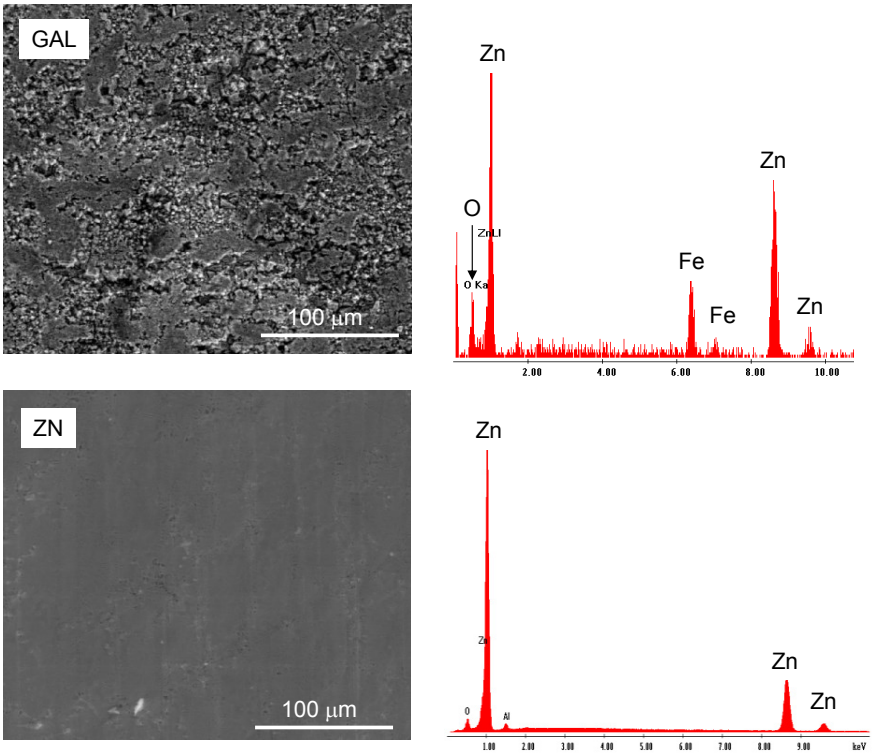


Fig. 1. SEM photographs (1,000X) and EDXS spectra of the tested substrates.

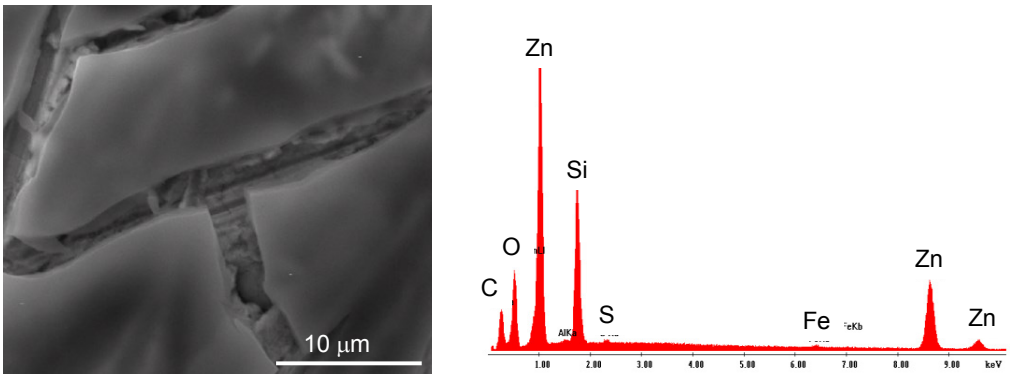


Fig. 2. SEM photograph (10,000X) and EDXS spectrum of a ZN sample pre-treated with MTMO.

3.2 Dry adhesion before corrosion testing

Adhesion testing by the Tape Test gave satisfactory results because in all cases the ASTM rating was 4B or higher, with less than 5% of removed area. However, the impact method, more demanding, revealed some differences. For both considered materials the MTMO pre-treated samples showed less paint film peeling than non treated ones, indicating that MTMO was a suitable adhesion promoter for zinc coatings. As well, the ZN samples with and without pre-treatment had a better performance than the GAL ones, Fig 3.

3.3 Aging in Humidity Chamber (HC)

In areas with intact paint film all the systems exhibited good protective behavior, no blistering, but loss of paint gloss and color, Fig 4. However, evaluated after the trial, the adherence in those areas showed marked differences, being the ZN-MTMO (Fig 5) the best-wet adhesion system.

Fig. 3. Samples after impact test.

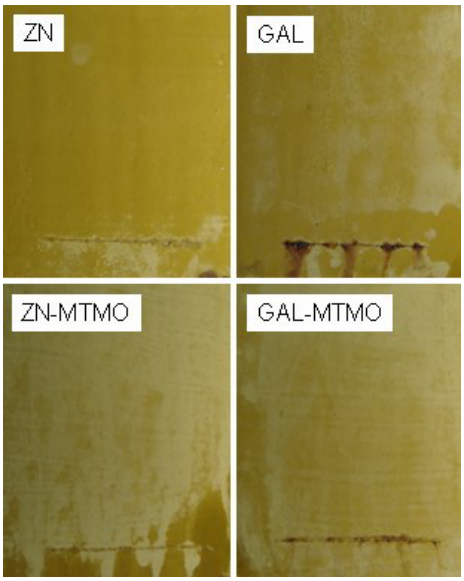


Fig. 4. Photograph of the samples after 42 days of exposure to CH.

Neither of the tested systems shows film delamination near the cut. However, in this area on GAL and GAL-MTMO samples the presence of steel corrosion products was observed (Fig. 6). This was probably due to its high content on the coating surface and not to the corrosion of the steel substrate. This coloration of the corrosion products was considered as purely cosmetic. However, many users consider these patches unacceptable from a qualitative point of view. On the ZN samples were observed the characteristic white corrosion products of zinc in this medium (Fig 6). As it is possible to see, the pre-treatment had an important effect reducing the amount of generated oxides, which means that, apart from being a suitable adhesion promoter, the MTMO provides a good

temporary protection against corrosion in the considered exposure conditions.

With regard to the EIS measurements carried out on the intact area of the samples periodically taken of from the HC, Fig 7 shows that the behavior of all the studied systems was quite similar.

Fluctuations in the impedance values occurring in some cases were attributed to the dynamic behavior of the interfacial processes taking place in these systems, since, when the electrolyte diffuses through the coating and reaches the metal substrate, the total impedance value may drop. However, due to its dielectric characteristic, most of the formed corrosion products seal these faults causing the impedance to increase again. As the exposure time increased, the trend in all cases was that the impedance module decreased, stabilizing at values close to $8x10^5$ Ωcm^2 at 42 days exposure. Such stabilization indicates that the deterioration process of the involved metal/paint system was very slow.

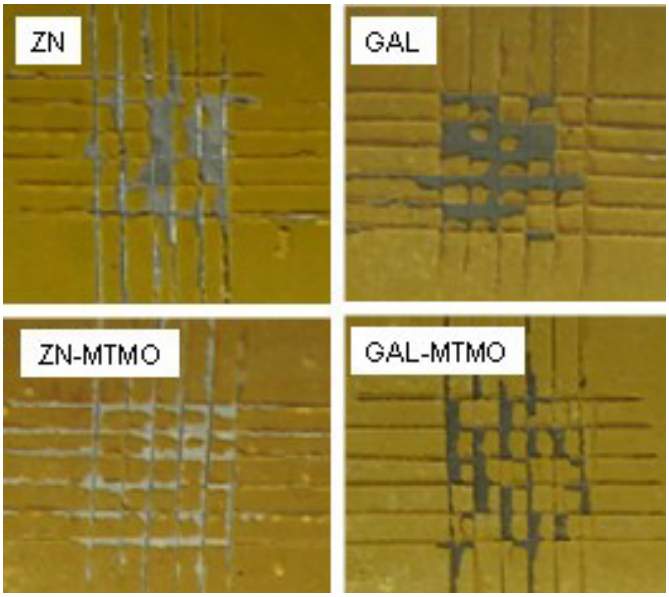


Fig. 5. Photograph of samples after the tape adhesion test after 42 days of exposure in HC.

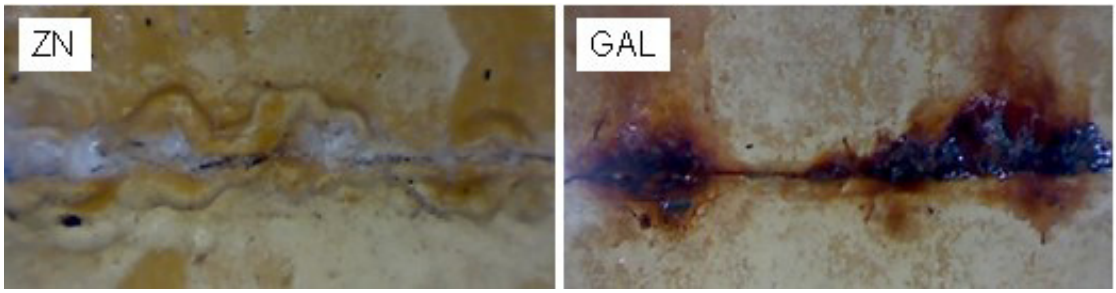


Fig. 6. Optical microscope photograph (50X) of the cutting zone of ZN and GAL samples after 42 days of exposure in HC.

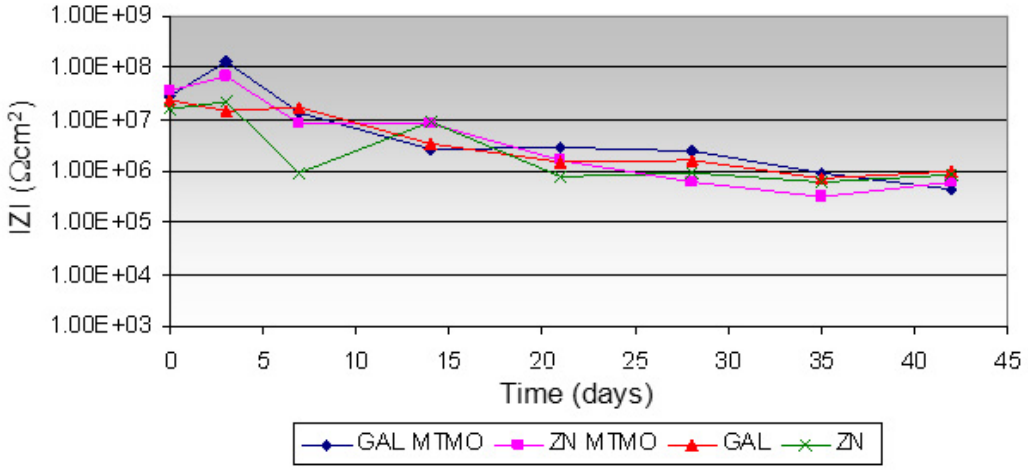


Fig. 7. Evolution of the impedance module at low frequency during exposure in HC.

3.4 Aging in Salt Spray Chamber (SSC)

In this test, clear differences were observed with respect to the blistering evolution from the cut. Delamination rate was nearly linear over 42 days testing. No pre-treated samples had a higher delamination rate, with values of 0.9 and 0.6 mm/day for GAL and ZN samples, respectively (Fig 8).

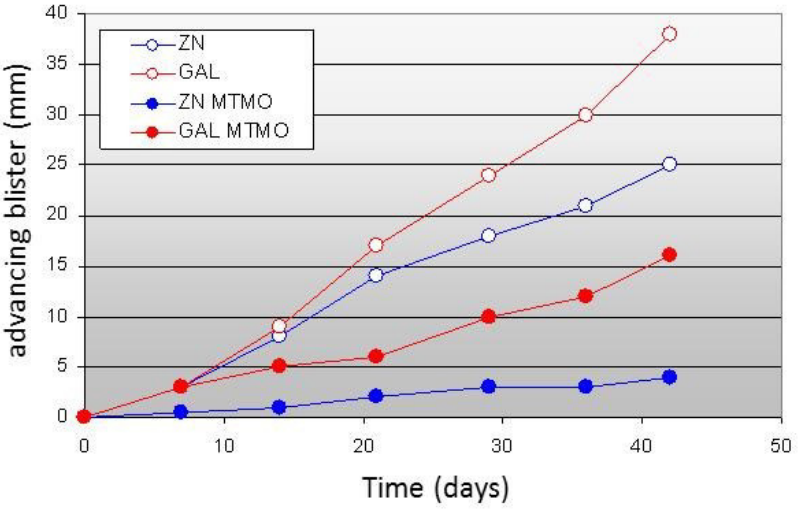


Fig. 8. Blistering evolution from the cut as a function of the exposure time in SSC.

The time dependence of the coating delamination on GAL samples was particularly attributed to the formed steel corrosion products identified in this medium by Almeida *et al.* as maghemite (γFeO_3), and in a lesser extent by the Zn one characterized as simonkolleite ($Zn_6(OH)_8Cl_2.H_2O$) [Almeida et al. (2000)]. In ZN samples the corrosion products were mainly constituted by simonkolleite [Díaz Rodríguez (2001), Seré et al. (1998)]. Since the iron corrosion products are more voluminous than the zinc ones, the pressure within the blister increases causing adhesion loss and, consequently, paint delamination in its edge (Fig. 9). The corrosion products morphology and EDXS spectra for both samples are shown in Fig 10.

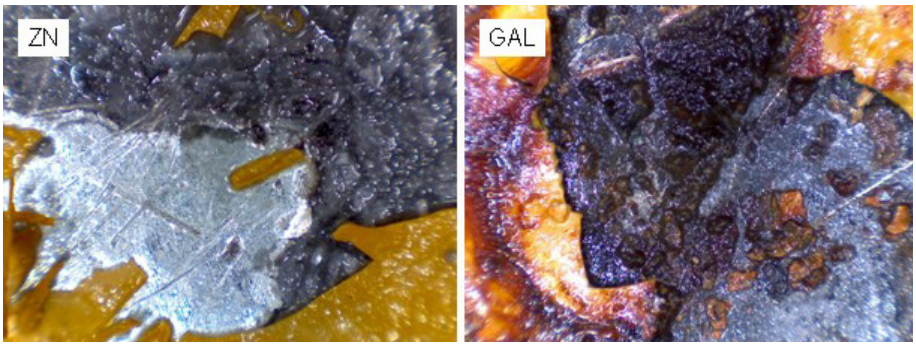
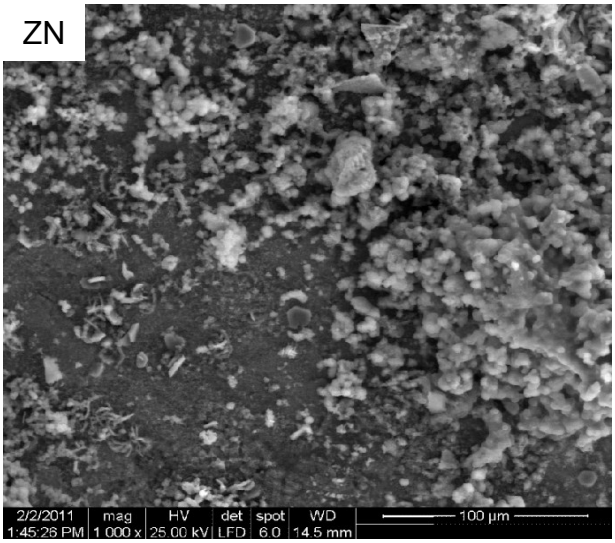
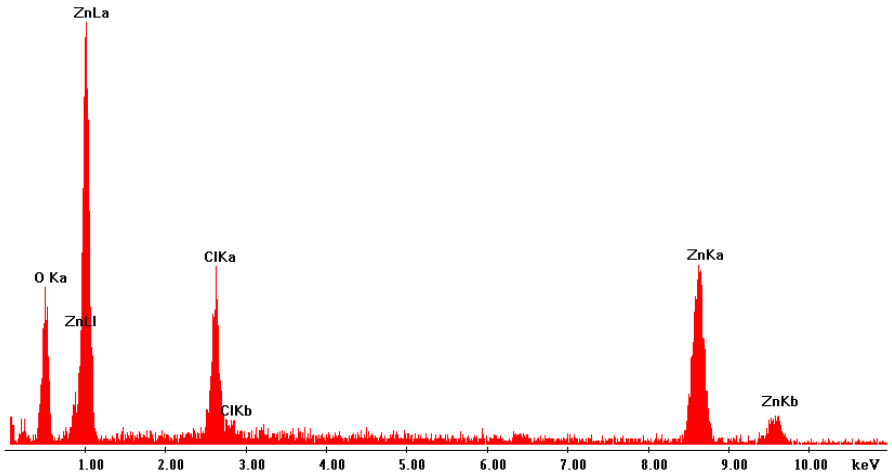


Fig. 9. Photographs taken with an optical microscope (50X) of samples exposed 42 days in SSC. Edge of blister pick up with a cutting element.





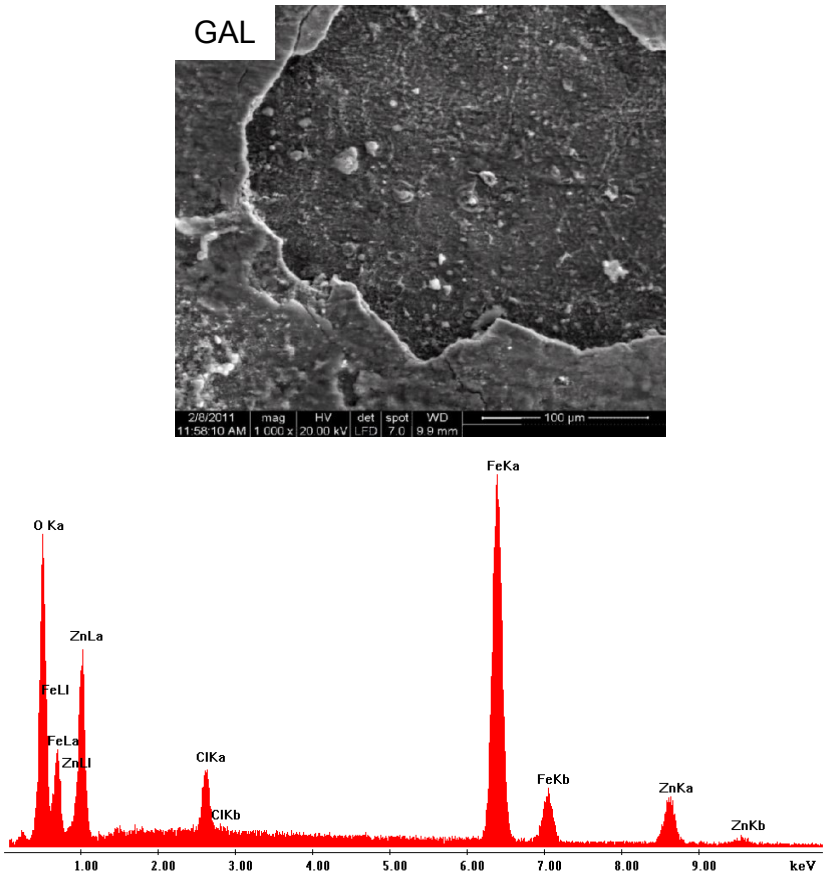


Fig. 10. SEM photographs and EDXS spectra of the area adjacent to cutting. Samples exposed 42 days in SSC

The periodical evaluation by EIS showed differences in the impedance modulus evolution at different test times (Fig 11). The best performance corresponded to the ZN-MTMO samples since even though there was a decrease of |Z| after 15 days of test, the values remained high throughout the test. The poor protective behavior was exhibited by the samples without treatment. In those cases, the decrease of the impedance module was very significant, reaching values similar to those of uncoated zinc before the 30 days of test. This behavior difference was ascribed to the fact that, in samples without pre-treatment, the electrolyte reached the substrate due to adhesion failures in some isolated places where small blisters were formed, significantly reducing the system impedance.

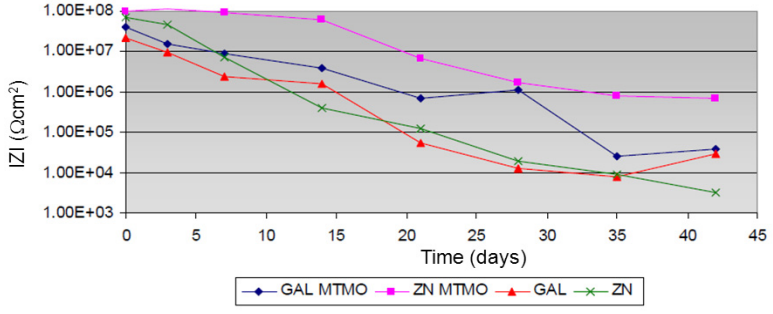


Fig. 11. Evolution of the impedance module at low frequency during exposure in SSC

4. Conclusions

The obtained results allow concluding that MTMO is a good adhesion promoter between water-based polyurethane paints and both considered substrates (galvanized steel or Galvanneal) at the present exposure conditions. In media with high humidity but without contaminants (HC) all the duplex systems behaved well, and without blistering or delamination after 42 days of exposure. However, in the case of Galvanneal, the presence of iron in the corrosion products brings up a reddish color, affecting the aesthetic appearance of the paint/Galvanneal system. The MTMO pre-treatment decreased the formation of corrosion products in areas where the paint film was artificially damaged.

In presence of aggressive Cl^- ions (SSC) there was a significant delamination from the cut made in the organic coating prior to testing. The best performance was shown by MTMO pre-treated samples. No pre-treated Galvanneal samples had a poorer performance because the corrosion products formed under the blister consist mainly of iron oxides, which are very bulky and cause the rapid progress of paint delamination. The EIS results agree with those obtained by visuals observation. This indicates that this is a powerful tool for assessing the corrosion of these systems.

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