Int. J. Electrochem. Sci., 10 **(2015)** 4654 - 4665

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Technical Note

Characterization of Corrosion Behavior of Painted Galvanized Steel under Accelerated Conditions.

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Received: 1 December 2014 / *Accepted:* 23 March 2015 / *Published:* 28 April 2015

In the present study three systems of carbon steel (1008) are evaluated, which were provide of two corrosion control methods, barrier and cathodic protection (painted and galvanized respectively) commonly used in the construction industry. They were evaluated under accelerated conditions exposed in fog chamber, according to ASTM B-117, which specifies continues exposition of sodium chloride at 5% and 35 °C. The main aim of the research was to characterize the corrosion resistance and to determine the degradation mechanism under test's conditions. The results after 1080 and 3500 hours of exposure are presented, with adhesion measure (ASTM D-3359) and scratch resistance measure (D-1654) for each exposure time, as well as the characterization of corrosion attack through the mapping analysis of Scanning Electron Microscope / Energy Dispersive X-ray. According to the results it is proposed that the corrosion of the systems under study begins at galvanized – metal base interface. Later advances due to formation of porous layer of zinc hydroxi-chloride, which it's characteristic of environments with chloride ions, forming zinc's corrosion products like zinc oxide and zinc hydroxide on the porous layer until iron starts to dissolve, producing iron oxide and iron oxy-hydroxide on the zinc's corrosion products and porous layer.

Keywords: Corrosion Mechanism, Carbon Steel 1008, Painted Galvanized, Accelerated Tests.

1. INTRODUCTION

The atmospheric corrosion, potentially destructive consuming sources and time, is the electrochemical process in which metals are deteriorate by atmospheric factors, that include the effect of climate conditions (periods of wetting and drying, temperature, humidity, rainfall, wind speed and direction, solar and ultraviolet radiation) and the effect of pollution (SO_2, NaCl, CO_2, NO_x and solid particles). Another factor is that atmospheric corrosion involves chemical, electrochemical and physical process in three mater states (solid, liquid and gaseous) and two interfaces (solid/water and water/atmosphere) [1-6].

Due to excellent performance against atmospheric corrosion, zinc has been historically used as a steel coating; therefore studies have been done to understand the mechanisms of its atmospheric interaction. The zinc protection is given by its galvanic action, when a discontinuity exists in the coating a dense and adherent corrosion product layer forms and fills it [7-11].

With the galvanized and the paint the steel is protected of corrosion, through forming patina layer in the galvanic coat; at the beginning zinc oxide and zinc hydroxide are formed, later they interact with carbon dioxide of the environment to produce zinc carbonate which is a passive and stable layer that adhere at surface and is unsolvable. This layer corrodes very slowly. Also zinc is anodic to steel, so galvanic coat provides cathodic protection, as well as paint separates galvanized steel of the corrosive media providing barrier protection [12-15].

Metal’s corrosion has an important economic impact. Corrosion’s cost studies have been done by several countries. Although the methodology varies, all estimate the annual cost and its percent of gross national product. In the period from 1999 to 2001 a more systematic study was performed in the U.S. the cost of corrosion was determined to be 3.1 percent of the gross domestic product [16].

Table 1. Overview of cost-of-corrosion studies by country [16].

Country	Annual corrosion’s cost Billion	% GNP	Year
United States	$ 5.5	2.1	1949
India	$ 320	-	1960
Finland	$ 54	-	1965
West Germany	$ 6	3	1967
United Kingdom	£ 1,365	3.5	1970
Japan	$ 9.2	1.8	1974
United States	$ 70	4.2	1975
Australia	$ 2	1.5	1982
Kuwait	$ 1	5.2	1987
United States	$ 276	3.1 (GDP)	2002

2. EXPERIMENTAL PROCEDURE.

In order to develop the present study we establish the next experimental procedure, with the aim of identify the degradation mechanism of the three systems of painted galvanized steel, through the characterization of corrosion behavior relative to localized attack causes by accelerated test according to ASTM B-117 [17].

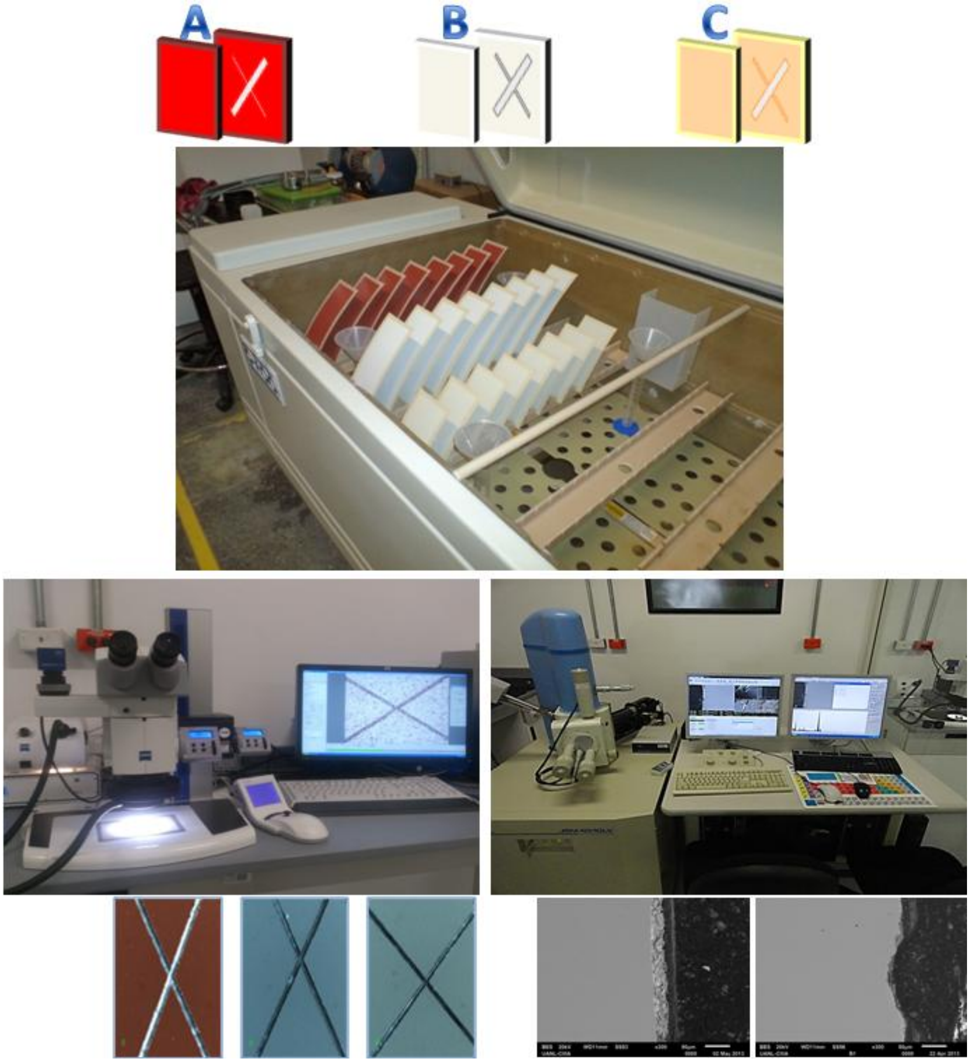


Figure 1. Scheme of the experimental procedure.

Three systems (A, B and C) are prepared to test in fog chamber, which include the sample cut (10 x 15 cm) and the mechanical scratch according to ASTM D-3359 “A” method [18]. Then are tested in fog chamber during 1080 and 3500 hours. After that are evaluated superficially with adhesion and scratch resistance clasifications according to ASTM D-3359 [18] and ASTM D1654 [19] respectively. Finally are analized in the three layers substrate, galvanized and painted with Scanning Electron Microscope / Energy Dispersive X-ray technique in cross section.

Material. The study material is a carbon steel AISI 1008 provided of two corrosion control methods, cathodic protection (galvanic coating) and barrier protection (paint coating). Given that we have three systems (figure 2):

- A – Galvanic coating (Z275~20µm) and red siliconized polyester coating (25µm).
- B – Galvanic coating (Z180~14µm) and white polyester coating (38µm).
- C – Galvanic coating (Z275~20µm) and beige siliconized polyester coating (25µm).

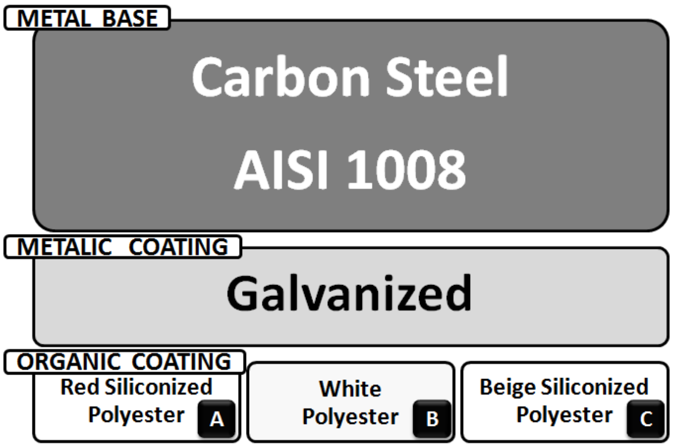


Figure 2. Materials under study.

Samples preparation. The samples were cut in panels of 10 x 15 cm, and the edges were covered with tape to avoid corrosion there. Besides a mechanical scratch was done according to ASTM D-3359 "A" method [18].

Accelerated test. The test was carried out according to ASTM B-117 [17]. Which specifies a continue exposition in fog chamber of sodium chloride at 5% and 35 °C.

Stereoscope. In order to evaluate the adhesion (ASTM D-3359) [18] and scratch resistance (ASTM D-1654) [19] of the organic coating for the three systems after accelerated test, a stereoscope was used to take photomicrographs of the specimen's surface.

Scanning Electron Microscope (SEM). In order to characterize the three systems after exposure in fog chamber a SEM was used to determine the attack morphologies. Corrosive agents were identified through Energy Dispersive X-ray technique using the elemental distribution mapping (EDAX) [20].

3. RESULTS AND DISCUSSION.

After expose the three materials in accelerated conditions during 1080 and 3500 hours, we obtained the next results.

In 1080 exposure hours, the organic coating was detached of the galvanized due to corrosion attack. The figure 3 shows the surface of the system "A" sample with siliconized polyester coating. By

Scanning Electron Microscope (SEM) the cross section is observed, where chlorine presence is found in scribed zone as well as non scribed zone and titanium absence which indicates the paint loses; besides this analysis is corroborated with the elements distribution mapping where the corrosion attack is shown in the galvanized – metal base interface.

In the figure 4 can be observed the surface of the system “B” sample (polyester coating) after 1080 exposure hours. The organic coating remains, which indicates that the system does not suffer attack by corrosion. In the photomicrographs obtain by SEM the cross section is observed, where chlorine presence is not found in both zones (with and without scribed) this confirms the photomicrographs seen with stereoscope; additionally it can be corroborated with the elements distribution mapping.

In the morphologies obtained by SEM the cross section of the system “C” sample (siliconized polyester coating) is shown, figure 5, after 1080 exposure hours. Where chlorine presence is found only in scribed zone, this confirms the stereoscope results with surface photomicrographs; also it can be validated with the elements distribution mapping where the corrosion attack appears in the galvanized – metal base interface.

The system “A”, after 3500 exposure hours, the siliconized polyester organic coating was almost completely detached of the galvanized due to corrosion attack. In the figure 6 can be observed this deteriorate and in the cross section chlorine and oxygen presence is found in the scribed zone and chlorine in the zone without scribed; besides this analysis can be corroborated with the elements distribution mapping where the corrosion attack by chlorine is shown in the galvanized – metal base interface and by oxygen in the metal base in the scribed zone.

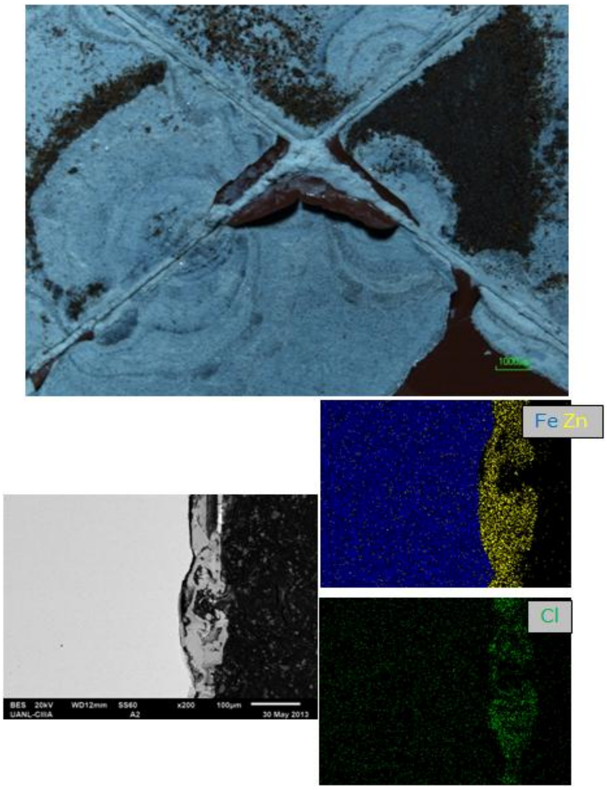


Figure 3. System A after 1080 hours in FC.

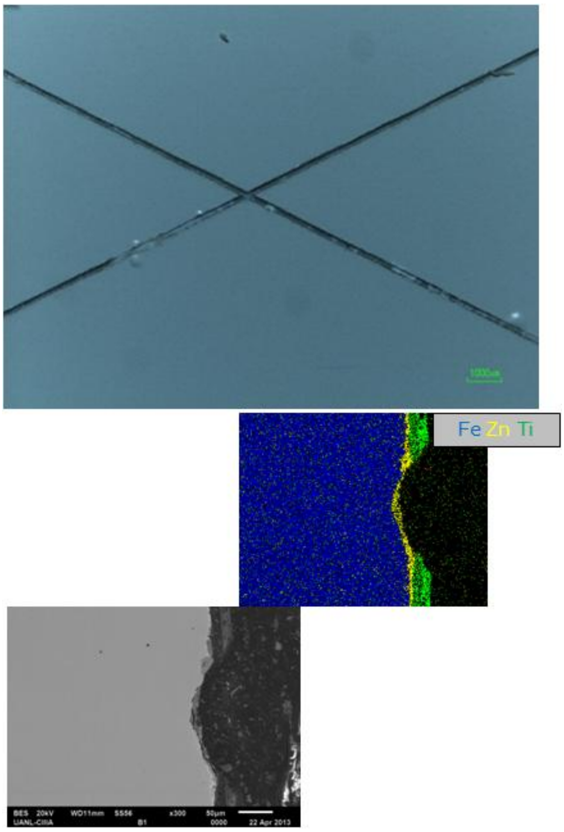


Figure 4. System B after 1080 hours in FC.

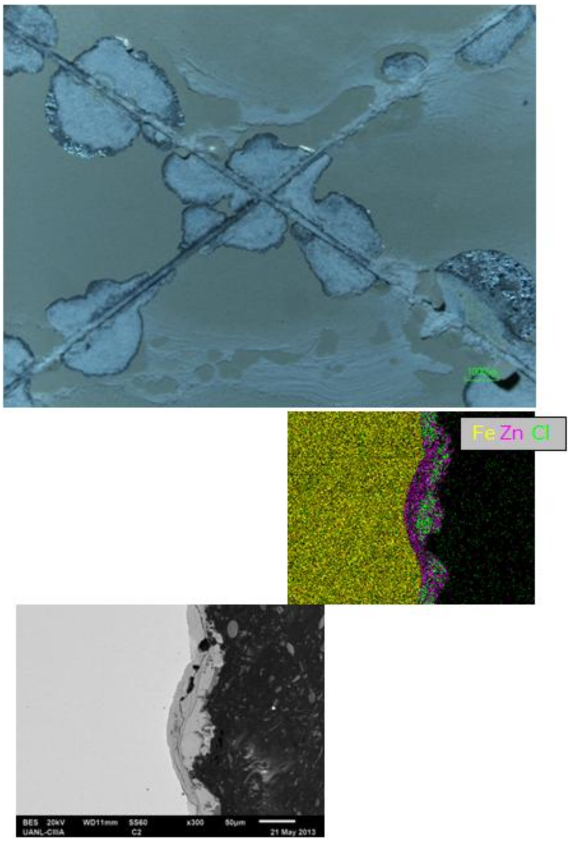


Figure 5. System C after 1080 hours in FC.

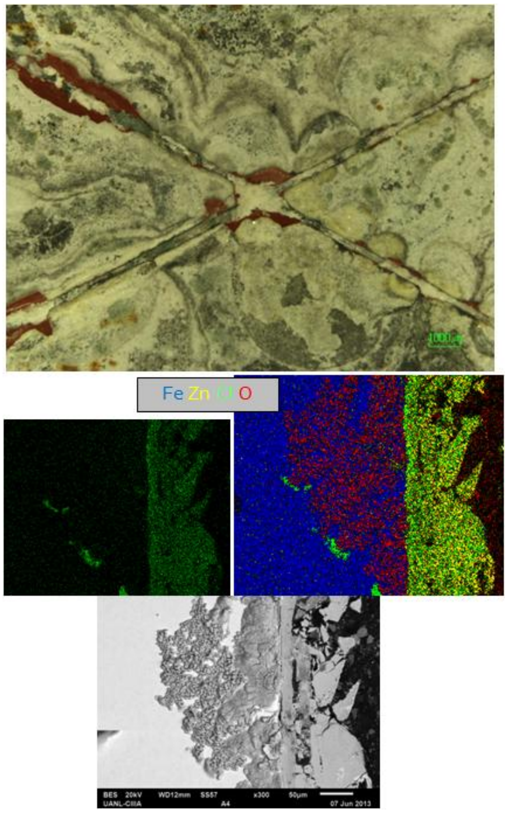


Figure 6. System A after 3500 hours in FC

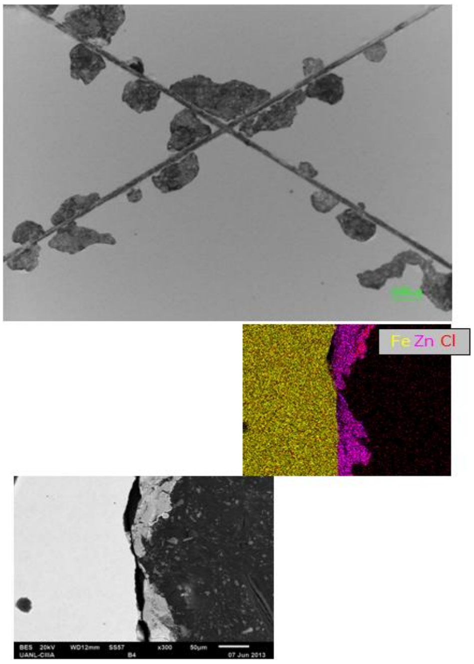


Figure 7. System B after 3500 hours in FC.

The system "B" can be observed in the figure 7, after 3500 exposure hours. The polyester organic coating remains in the majority of the surface, which indicates that the paint does not allow that chlorine goes inside to reach at galvanized – metal base interface. The analysis in cross section by

Scanning Electron Microscope does not find the chlorine presence in the zone without scribed but it find a few in the scribed zone, without causing the organic coating detaches of galvanized. This confirms the photomicrographs seen with stereoscope; additionally it can be validated with the elements distribution mapping.

In the figure 8 can be observed the surface of the system "C" sample after 1080 exposure hours, the siliconized polyester organic coating was detached on the entire evaluated surface of the galvanized due to corrosion attack. In the photomicrographs obtain by SEM the cross section is observed, where chlorine presence is found in both zones (with and without scribed) as well as the absence of titanium which indicates the paint loses, besides this analysis is corroborated with the elements distribution mapping where the corrosion attack is shown in the galvanized – metal base interface.

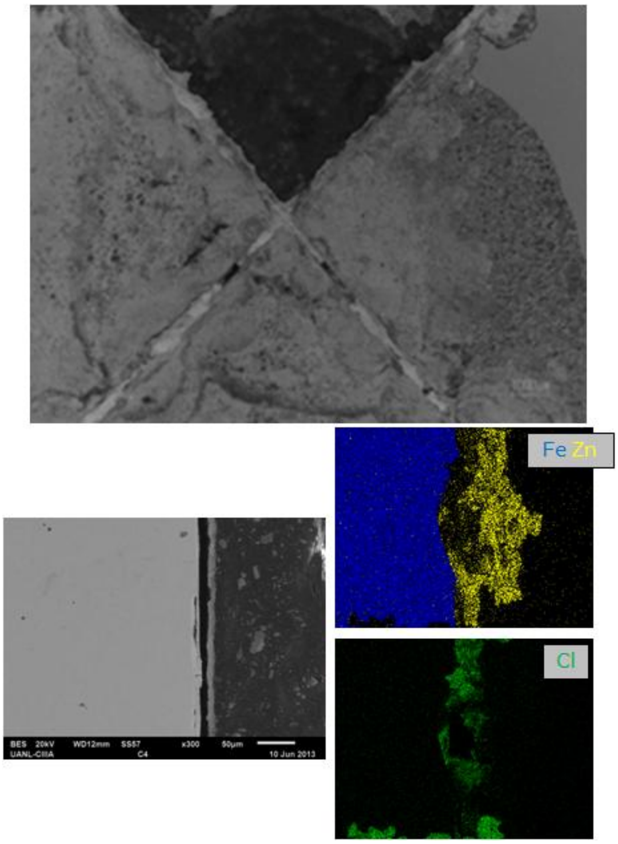


Figure 8. System C after 3500 hours in FC.

The analyze of the results in fog chamber allows to establish that system "B" gives better resistance than "A" and "C" to corrosion attack avoiding the electrolyte permeability through organic coating for 3500 exposure hours according to ASTM B-117 [17].

Based on the norms employed and using the photomicrographs obtained by stereoscope, classification of adhesion by "A" method and scratch resistance were evaluated for each system "A", "B" and "C" with its respective exposure time. Obtaining the next results.

Table 2. Systema A.

Exposure Time	Mean Distance	Clasification	
		Scratch resistance	Adhesion A method
0	*0.213 mm*	*10*	*5*
1080 hrs	*15.346 mm*	*1*	*0*
3500 hrs	*27.165 mm*	*0*	*0*

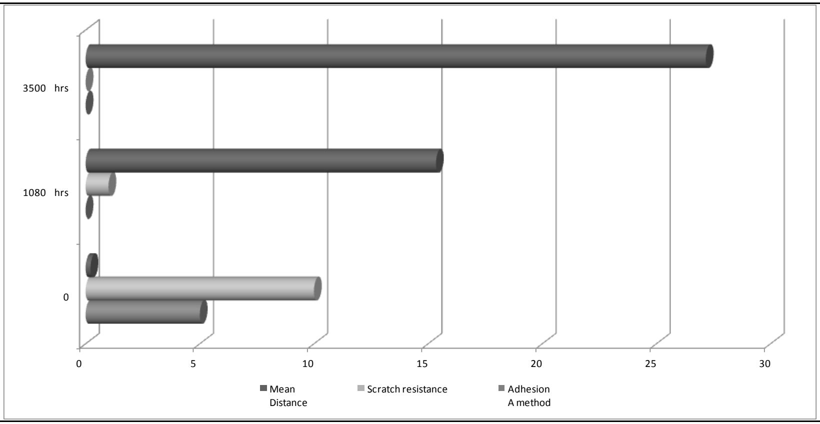


Table 3. System B.

Exposure Time	Mean Distance	Clasification	
		Scratch resistance	Adhesion A method
0	*0.176 mm*	*10*	*5*
1080 hrs	*0.195 mm*	*9*	*5*
3500 hrs	*2.495 mm*	*7*	*3*

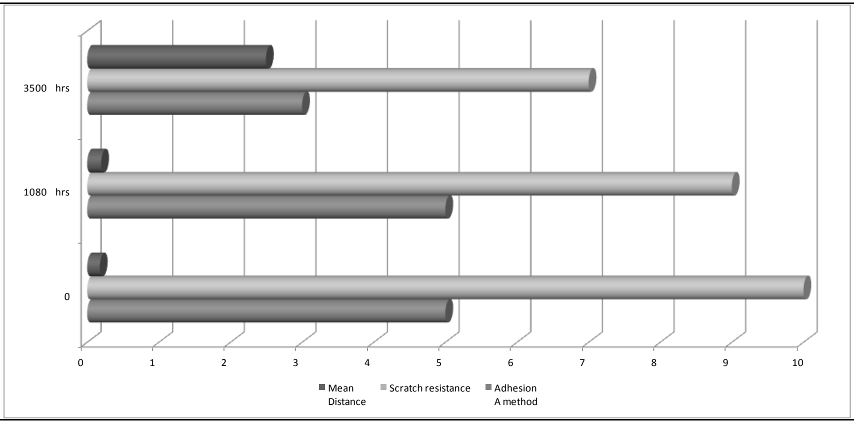
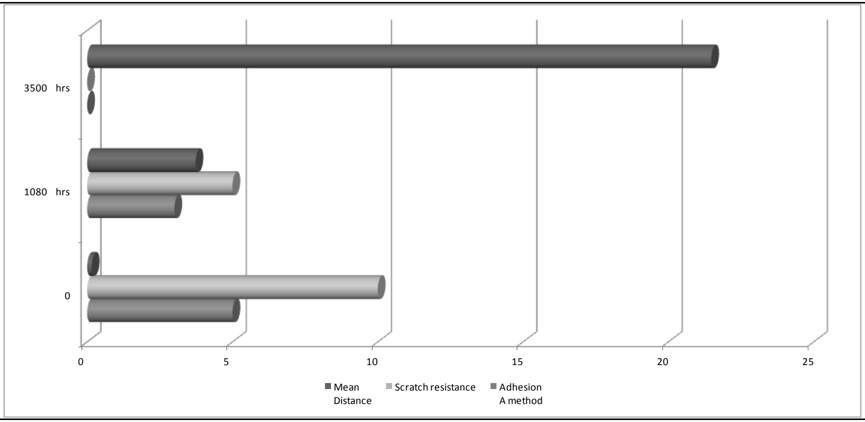


Table 4. System C.

Exposure Time	Mean Distance	Clasification	
		Scratch resistance	Adhesion A method
0	*0.158 mm*	*10*	*5*
1080 hrs	*3.73 mm*	*5*	*3*
3500 hrs	*21.48 mm*	*0*	*0*



System “B” shows positive results to scratch resistance and adhesion until 3500 exposure hours, while system “A” and “C” show unacceptable results at 1080 and 3500 hours respectively.

For the three systems under study, we propose the next corrosion mechanism which it’s divide in three phases. In the first phase zinc dissolves in active way, reacts with chlorine of electrolyte and produces zinc chloride which continues reacting producing now zinc hydroxide that finally in presence of chlorine ion and proton form zinc hydroxi-chloride. In marine atmospheres is common to found this corrosion product for galvanized steel. This corrosion product is porous and allows the solution permeability [21, 22].

$$\begin{aligned}
&Zn^{++} + 2NaCl + H_2O + \tfrac{1}{2}O_2 \leftrightarrow ZnCl_2 + 2NaOH \\
&ZnCl_2 + H_2O + \tfrac{1}{2}O_2 + 2H^+ \leftrightarrow Zn(OH)_2 + 2HCl \\
&HCl + NaOH \leftrightarrow NaCl + H_2O \\
&5Zn(OH)_2 + 2H^+ + 2Cl^- \leftrightarrow ZnCl_2 4Zn(OH)_2 + H_2O
\end{aligned}$$

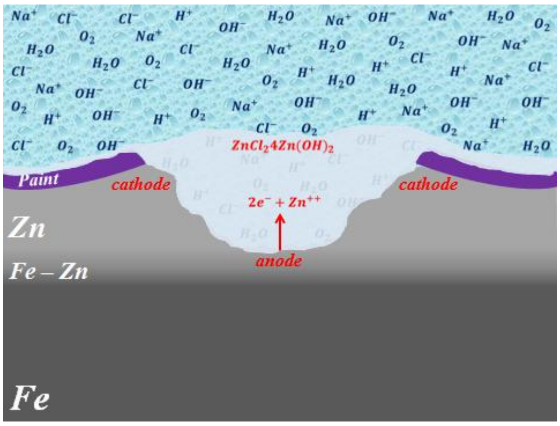


Figure 8. Zinc hydroxi-chloride formation.

The second phase of the propose mechanism happens through the porous layer of zinc hydroxi-chloride. It begins with zinc dissolution that reacts again with chlorine in the electrolyte producing zinc chloride which in turn produces zinc hydroxide [23] and it's deposited on the porous layer. Zinc also reacts with oxygen to produce zinc oxide deposited on the porous layer too [24].

$$\begin{aligned}
&Zn^{++} + 2NaCl + H_2O + \tfrac{1}{2}O_2 \leftrightarrow ZnCl_2 + 2NaOH \\
&ZnCl_2 + H_2O + \tfrac{1}{2}O_2 + 2H^+ \leftrightarrow Zn(OH)_2 + 2HCl \quad 2Zn^{++} + O_2 \leftrightarrow 2ZnO \\
&HCl + NaOH \leftrightarrow NaCl + H_2O
\end{aligned}$$

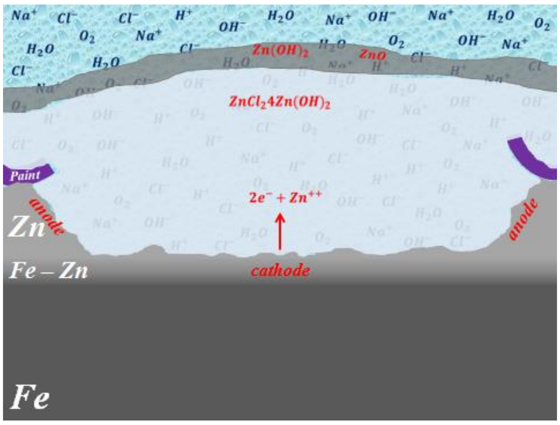


Figure 9. Zinc oxide and zinc hydroxide formation.

In the third and last phase of this propose mechanism, iron starts to take part of the process. First iron and zinc dissolve in the porous layer, iron reacts with chlorine of the solution to produce iron chloride, while zinc continues reacting and producing zinc oxide and zinc hydroxide.

Iron chloride continues reacting to produce ferric oxide [25] and iron oxy-hydroxide [26, 27] both iron corrosion products are deposited on the zinc corrosion products.

$$
\begin{aligned}
&Fe^{++} + 2NaCl + H_2O + \tfrac{1}{2}O_2 \leftrightarrow FeCl_2 + 2NaOH \\
&2FeCl_2 + 2H_2O + \tfrac{1}{2}O_2 \leftrightarrow Fe_2O_3 + 4HCl \\
&FeCl_2 + H_2O + \tfrac{1}{2}O_2 + H^+ \leftrightarrow FeOOH + 2HCl \\
&HCl + NaOH \leftrightarrow NaCl + H_2O
\end{aligned}
$$

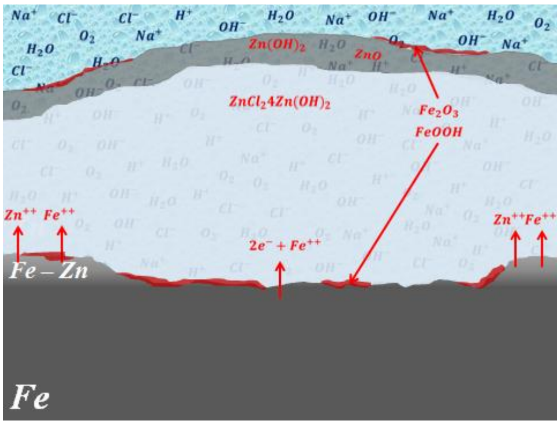


Figure 10. Ferric oxide and iron oxy-hydroxide formation.

5. CONCLUSIONS.

The accelerated corrosion test in fog chamber allows evaluating effectively the degradation mechanisms for the three systems under study in this research, managing to obtain a theory that describes the corrosion mechanisms present in ours systems.

The corrosion of the systems under study begins in the galvanized – metal base interface, and then advances through a porous layer of zinc hydroxi-chloride characteristics of environments that contain chlorine ions. Also zinc dissolution produces zinc oxide and zinc hydroxide on the porous layer. Finally iron starts to dissolve forming ferric oxide and iron oxy-hydroxide on the zinc corrosion products. The propose corrosion mechanism for painted galvanized steel in fog chamber with sodium chloride at 5% is coherent with the results obtained by SEM characterization as can be observed in the elements distribution mapping through EDAX technique.

System “B” shows positive results to scratch resistance and adhesion until 3500 exposure hours that can be seen by photomicrographs of surface taking with stereoscope, this can be ascribed to paint of the system “B” which doesn’t permit the electrolyte permeability avoiding the corrosion attack of the sodium chloride while system “A” and “C” show unacceptable results at 1080 and 3500 hours respectively.

ACKNOWLEDGEMENTS.
The authors thank to the Consejo Nacional de Ciencia y Tecnología in Mexico, for the economic support. We also thank to the academic body UANL-CA-316 "Deterioration and integrity of composite materials". As well as Rene Garza Cavazos, Antonio Maní Medrano and Hilario García Garza for their technical assistance.

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