We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

CLARIVATE ANALYTICS

BOOK CITATION INDEX

INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Improvement of the Electrochemical Behavior of 2024-T3 Alclad Using Polyester Coatings

Willian Aperador Chaparro

Additional information is available at the end of the chapter

1. Introduction

Organic coatings based on synthetic resins provide excellent corrosion protection after making a good cleaning and surface preparation, followed by a suitable pretreatment depending on the type of substrate to be protected (Atta, 2006, Atta, 2007; Sathyanarayan, 2008 .) Such protection systems can be applied in a single layer or multilayer, as in the case of coatings for aircraft industry, which are generally constituted by a pretreatment, a primer and a topcoat. Several studies concerning innovation and optimization of new alternative coatings corrosion protective aerospace application have been developed (Reynolds, 1997), researches have been oriented in two directions: first, alternative coatings to traditional surface treatment (pretreatment) , being the most representative case, the coatings by chemical oxidation from zirconium and titanium oxides (Sanchez-Amaya, 2007; Osborne, 2001; Neuder, 2003), and second, alternative coatings of traditional organic primers from resins and primers without any incorporation of cromatants pigments as corrosion inhibitors (Twite, 1998).

One of the disadvantages of the polyester-styrene copolymers has always been their tendency to shrinkage, which is due to the internal contraction of the molecule when the polymerization occurs. This has been improved with the addition of glass fibers or flakes and other fillings. However, substantial contraction can occur when a large area is coated with polyester resin and fiberglass, as in the case of the bottom of a tank or other structure. Therefore, the contraction should be a parameter to be considered during application (Munger, 1984; Groover 1997).

The adaptation of these protective corrosion systems requires a test to evaluate the performance of the material in realistic exposure conditions through or during or under diverse environments, and even more, to establish an estimate of the life span of the protection system. Salt Fog Spray Test (SFST) described by ASTM B117 is one of the most

widespread testing methods (ASTM B117, 2008). In this evaluation process, SFST, a particular coatings of Hetron 197-3 and polyester are exposed to a salt spray to imitate the artificial marine environment and exaggerated conditions of temperature and relative humidity. These accelerated aggressive atmospheric environmental conditions can be considered to evaluate the behavior of the corrosion protective coating system and to assess its efficiency in terms of durability.

The aim of this work is the implementation of protective coating Hetron 197-3 polyester type applied on substrates of aluminum alloy Alclad 2024-T3, which is used as barriers to corrosion. This type of substrate is widely used in manufacturing the battery compartment of T-41 Aircraft. The coatings were exposed to 0 and 2000 hours in aggressive atmospheric conditions (acidified saline medium). The degree of deterioration was compared in protection systems based synthetic resin (Hetron 197-3) and polyester. The morphology surface analysis was made using Scanning Electron Microscopy (SEM) to observe the damage generated by exposure to aggressive media. The electrochemical performance of the coatings was evaluated through Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization curves, polarization curves and Nyquist plots indicate that antacid polyester resin coating have the lowest value of current and corrosion rate with the system traditionally used in the aviation industry (Plating Process (Alclad), Conversion Coatings for Aluminum Alloys, chemical oxidation)

2. Experimental details and results

2.1. Material, experimental processes and characterization techniques

The coverings fuselage of the T41 aircraft as well as internal areas prone to corrosion, such as the battery compartment, are made of aluminum alloy 2024-T3 sheet whose chemical composition is shown in Table 1, plated with alloy 1230 in accordance with international specifications of ASTM B209 (ASTM, 2007) (Table 2), and corrosion protective coatings, paint base according to military standards for aviation (surface pretreatment, primer and finish paint). This protection system consists of a surface treatment, commercially called Alodine 5700 that generates a chromium-free conversion coating in a chemical solution composed of 80% of an inorganic component of oxyfluoride species of titanium, zirconium and silicon ($H_2TiF_6+ZrO(OH)(CO_3)_{0.5}+SiO_2$). Also owns 20% of an organic component poly-4-vinyl-phenol and amines, thus promoting an inorganic protective coating by conversion from an organometallic complex of zirconates, and a good bonding surface for subsequent coating organic, and second, a primer surface with epoxy primer cromatante base, being its main component an epoxy resin diluted under strontium chromate pigments as corrosion protection, and finally a topcoat (polyurethane) (Twite, 1998)

The protection system based on synthetic resin comprises the following stages of implementation: The pretreatment was performed chemically, initiating with a process of cleaning and degreasing with an acid detergent, based on a phosphoric acid at a temperature of 46 °C for 10 minutes, then etching was performed with NaOH at a concentration of 50 g/l dissolved in distilled water for 1 minute at a temperature of 52 °C,

finally generated anchor treatment with Alodine 5700 was applied in a thin layer of polyester resin Polisec 115, of 50 microns per flush, then homogenizing the coating over the entire area of application. The resin had a curing time of 20 minutes. To finish the process was applied a coating polyester resin compound antacid Hetron 197-3, which joined as a glass flake filler by 20% (weight/weight) with respect to the total weight and 2% (weight /weight) of catalyst on the total weight. Two systems were obtained, H1 = 1layer (100 μm), H2 = 2 layers (200 μm). These systems were compared with commonly used coating which is a combination of Alodine 5700, epoxy primer and polyurethane paint, this coating was called PP.

Chemical composition of the substrate (AA 2024) approx. 91 %Al										
									Others	
% Weight	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	unspecified others	Total
Minimum	-	-	3.8	0.30	1.2	-	-	-	-	-
Maximum	0.50	0.50	4.9	0,9	1.8	0.10	0.25	0.15	0.05	0.15

Table 1. Chemical composition of the substrate alloy (Al 2024)

Chemical composition of the clad (AA1230) approx.99 % Al								
							Others	
% Weight	Si +Fe	Cu	Mn	Mg	Cr	Zn	Ti	unspecified others	Total
	0.7	0.1	0.05	0.05	-	0.1	0.03	0.03	0.15

Table 2. Chemical composition of the clad alloy (Al 1230)

The specimens were subjected to ultrasonic cleaning process in an acetone bath and dried prior to trial. The coatings were evaluated in an acidified salt spray according to ASTM B117 (ASTM B 117, 2008) norms. The electrochemical characterization was performed on a Gamry equipment model PCI-4 using the techniques of Tafel polarization curves and electrochemical impedance spectroscopy at room temperature, using a cell consisting of a typical 3-electrode arrangement, the working electrode with an exposed area of 1 cm², a reference electrode of Ag / AgCl and as counter electrode a platinum wire, in a solution of NaCl to 3.5 weight.% (ASTM B 209, 2007). Measurements of Tafel polarization curves were obtained at a scan rate of 0.125 mV / s in a voltage range of -200 mV to +1200 mV vs. Ecorr. Nyquist diagrams were obtained by frequency sweeps in the range from 0.001 Hz to 100 kHz with sinusoidal signal amplitude of 10 mV (Aperador, 2010). A scanning electron microscope (SEM) of high resolution (JEOL JSM - 6490LV) was used to measure the thicknesses in cross section after a pre-coating by gold.

2.2. Scanning electron microscopy

The microstructural analysis obtained by scanning electron microscopy (Figure 1), together with EDS analysis used in chemical analysis (Table 3), confirms the formation of conversion

coating on Alclad substrate surface (aluminum alloy 1230) . The surface morphology observed by SEM (Figure 2) clearly illustrates the roughness generated by chemical oxidation and the characteristic values recorded EDS chemical composition of elements such as Zr, Ti, Al, F and O, proper treatment with Alodine 5700.The composition of 35% in C, verified the presence of an additional organic binder, which promotes chemical affinity with the organic coatings applied on plating Al1230.
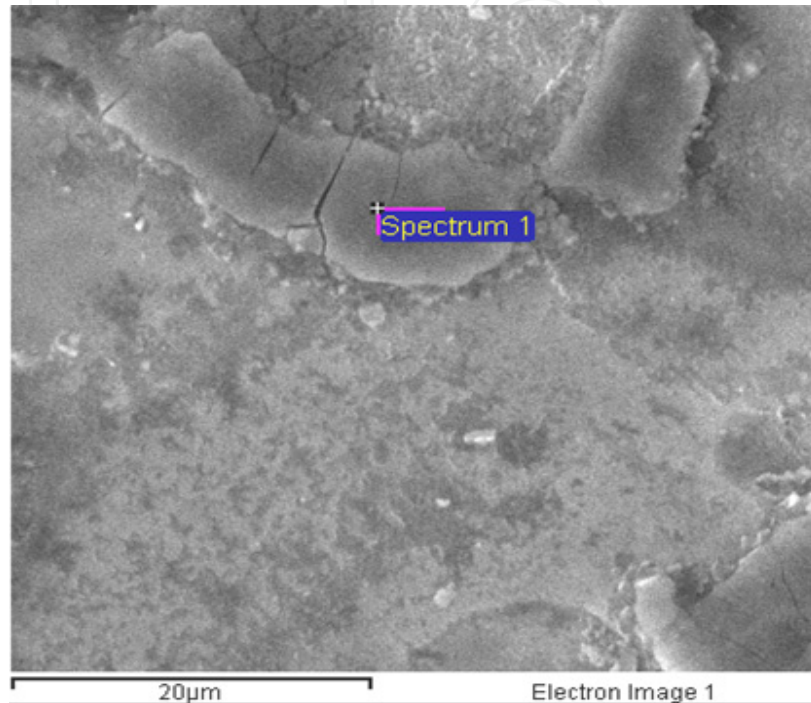

Figure 1. SEM micrograph which shows the region that performed the analysis of chemical composition by EDS to the surface of the substrate (AA 1230) prepared with Alodine 5700.

Element	Weight%	Atomic%
C	35.35	52.77
O	13.02	14.59
F	2.28	2.15
Na	0.24	0.18
Al	43.23	28.73
Si	0.22	0.14
Cl	0.11	0.05
K	0.20	0.09
Ti	1.18	0.44
Fe	0.10	0.03
Cu	0.22	0.06
Zr	3.87	0.76
Total	**100.00**	

Table 3. Chemical composition obtained by EDS for the surface of the substrate (AA 1230) prepared with Alodine 5700. The spectrum is shown in Figure 3.
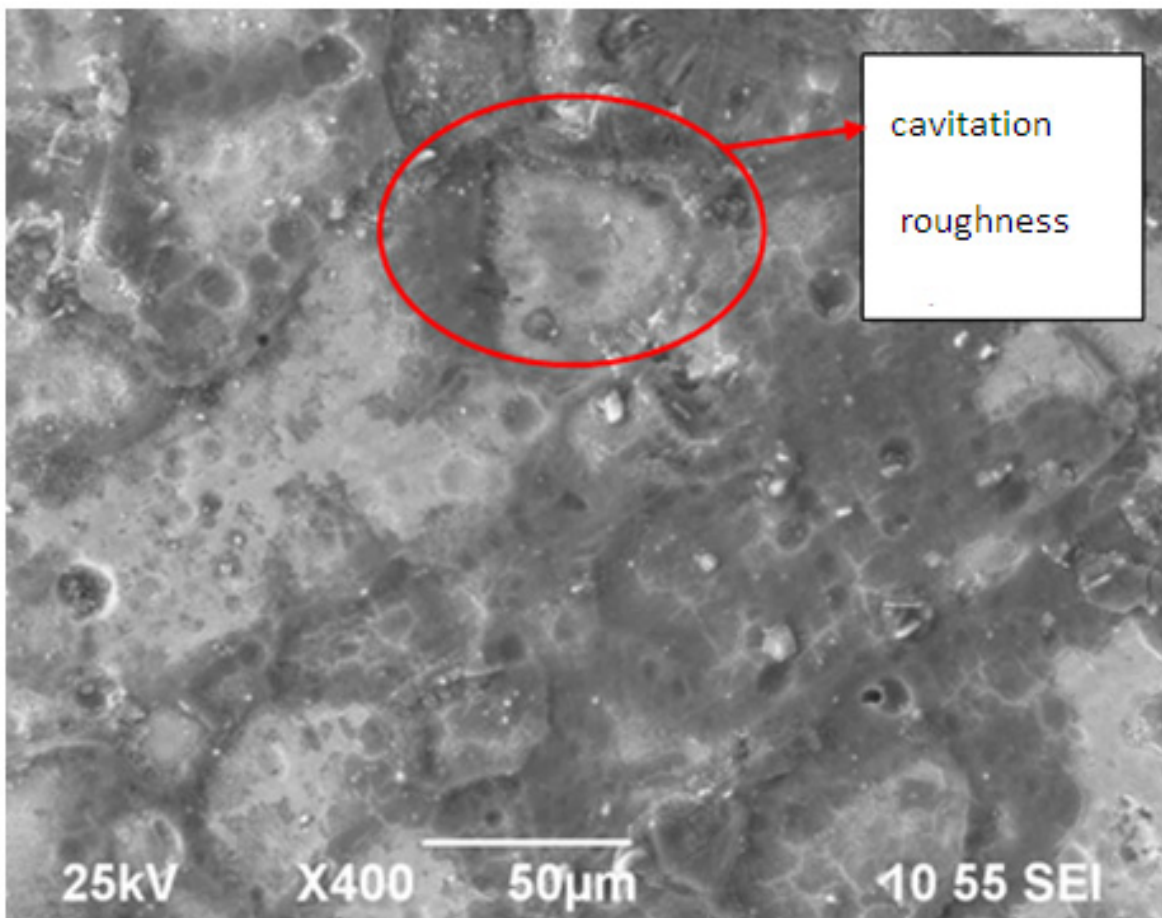
Figure 2. SEM micrograph of the substrate under chemical oxidation with Alodine 5700.

A scanning electron microcopy was used to determine the thickness of the coating, besides the conditions of the various layers and their thicknesses in the base polyester resin coating and Hetron 197-3 (Figures 3 and 4). However, for coating H2 can be seen an increase in the thickness of the antacid resin layer of about 50 microns after having been subjected to 2000 hours of exposure in the saline chamber, this is due to the permeability of the layer of polyester resin and a moisture retention in the molecular structure of the layer. In the micrographs of the H2 coating, it can be checked the continuous arrangement and parallel to the surface of the glass flakes simulating the shape of a surface veil and intensify the chemical barrier coating. Likewise there is a good cohesion of the layer to the substrate along the entire interface even after 2000 hours of salt spray exposure, corroborating a good anchor pattern (between the coating and substrate) despite the high viscosity of the resin.

2.3. Electrochemistry

Figure 5 shows the Tafel polarization curves for the coating polyurethane and polyester antacid resin (AH1, AH2 and PP). The polarization curves were obtained at 0 hours and 2000 hours. Found values of the anodic and cathodic slopes in each case, which are recorded in Table 4 along with values of current density, corrosion potential and corrosion rate for each of the cases were studied.
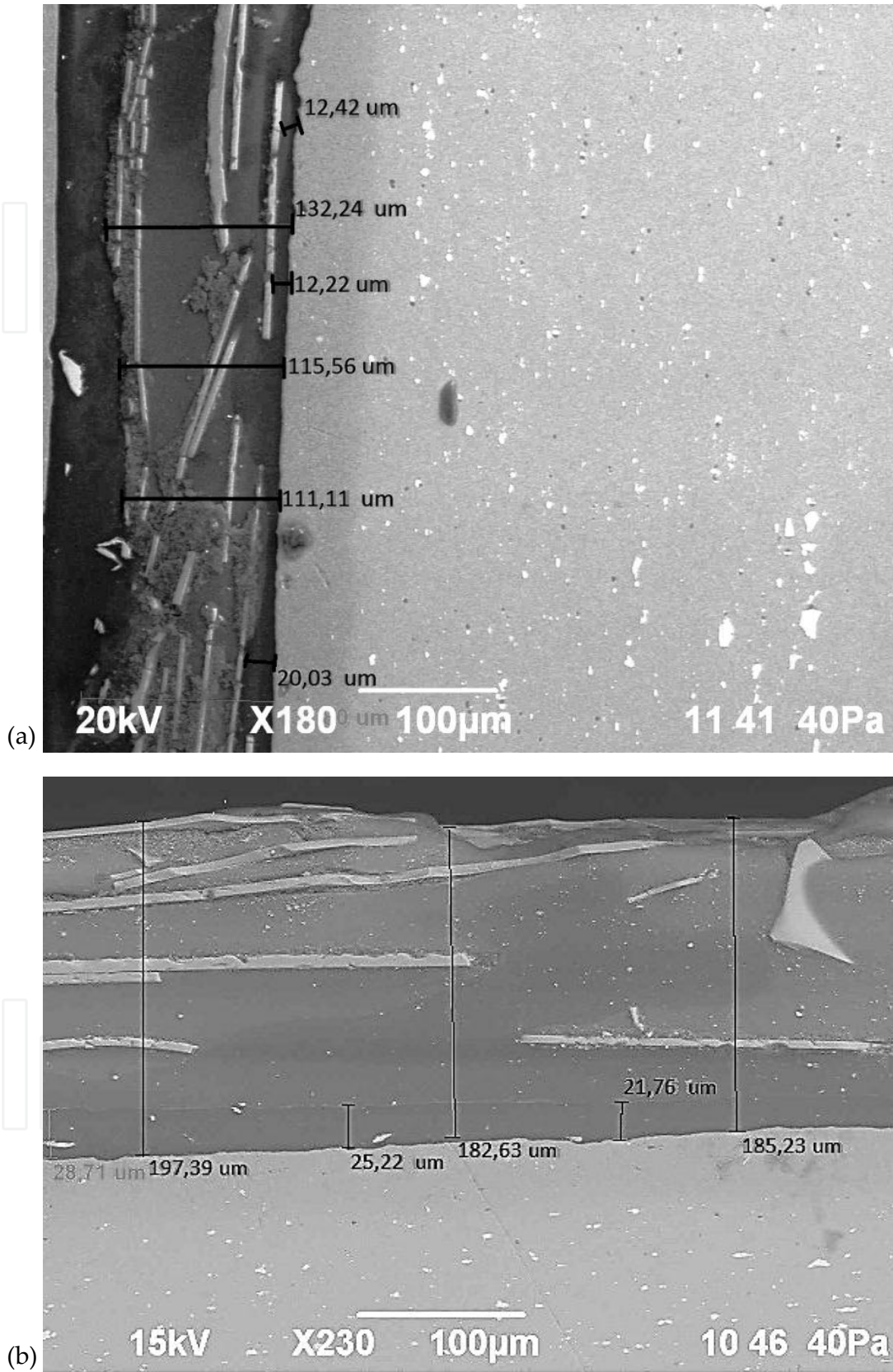
Figure 3. SEM micrographs of the H2 coating after exposure to salt chamber for (a) 0 hours and (b) 2000 hours.
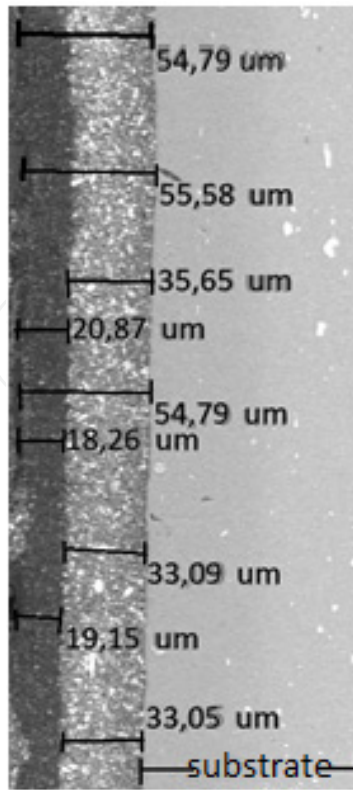
Figure 4. SEM micrograph of the PP coating after exposure to salt chamber for 2000 hours
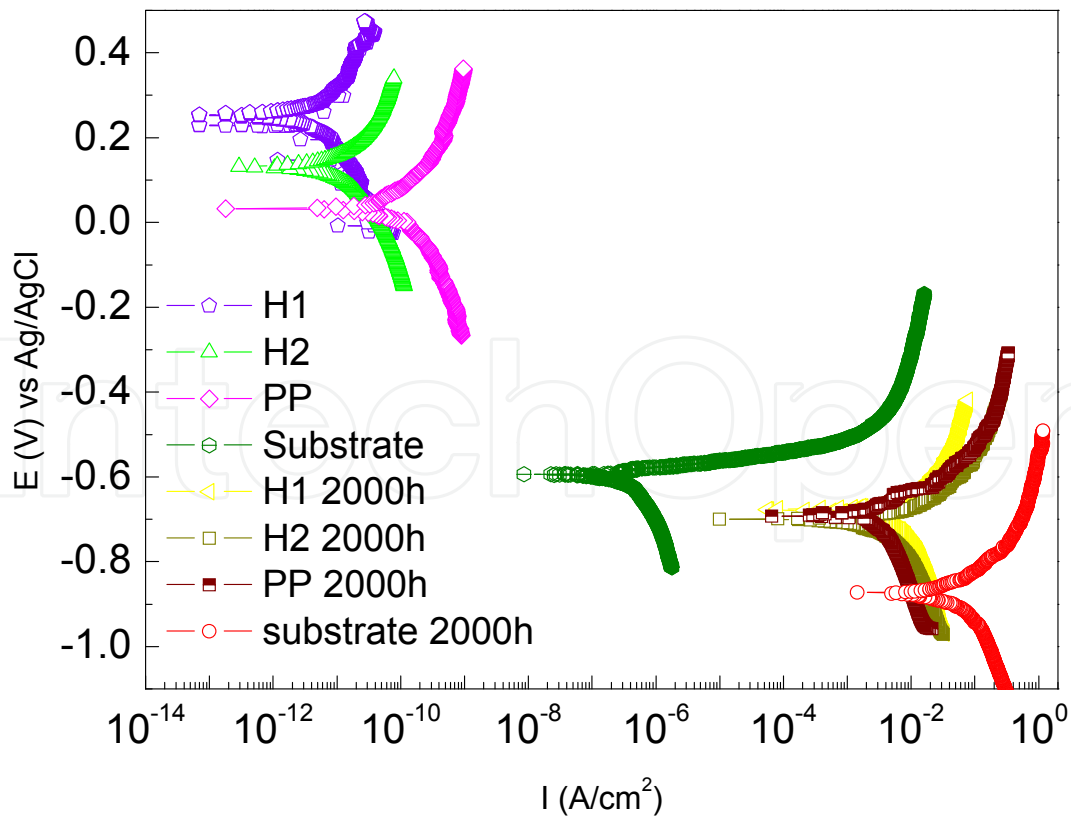

Figure 5. Tafel polarization curves of the substrate and coating types PP and H, evaluated in the salt chamber at 0 and 2000 hours.

The corrosion rate indicates a good performance of the coatings compared to the substrate, for 0 hours of exposure in the salt chamber. The coatings which have a lower density value of corrosion are called H with 1 and 2 layers, followed by those used by the military aviation industry. Subsequently, measures of Tafel polarization curves for 2000 hours of exposure to saline-acidified were performed. One can observe the increase in corrosion rate of the coating and the substrate showing the destructive effect of the medium exposed. Also it distinguishes the protective effect of the coatings compared to the substrate under these conditions. The lowest values of the corrosion rate were reported at (2.31×10^{-9} μmy) for PP coating. However, the coatings implemented in this study show a similar behavior to PP, the Nyquist plots corresponding to the substrate and coatings polyurethane type and synthetic resin exposed to 0 hours and 2000 hours.

	Substrate	H1	H2	PP	Substrate 2000h	H1 2000h	H2 2000h	PP 2000h
Anodic beta (V/decade)	$28,70 \times 10^{-3}$	145×10^{-3}	30×10^{-3}	387×10^{-3}	$497,1 \times 10^{-3}$	$79,80 \times 10^{-3}$	$510,1 \times 10^{-3}$	$239,7 \times 10^{-3}$
Cathodic beta (V/decade)	263×10^{-3}	245×10^{-3}	77×10^{-3}	389×10^{-3}	$737,2$	$178,9 \times 10^{-3}$	$475,0 \times 10^{-3}$	$371,5 \times 10^{-3}$
Corrosion current (A/cm^2)	370×10^{-9}	121×10^{-12}	3.31×10^{-12}	210×10^{-12}	$38,30 \times 10^{-6}$	$1,790 \times 10^{-6}$	$13,30 \times 10^{-6}$	$40,90 \times 10^{-9}$
Corrosion potential (mV vs Ag / AgCl)	-594	133.4	250	37,10	-686	-710	-740	-750
Corrosion rate (μmy)	4.03×10^{-6}	2.66×10^{-11}	3.60×10^{-11}	2.29×10^{-9}	443.8	20,71	15.41	$1,86 \times 10^{-2}$

Table 4. Electrochemical parameters generated from the Tafel polarization curves.

Table 4 and Fig.5 showing the decrease in the corrosion potential when the specimens have been subjected to half-acidified saline for 2000 hours, indicating active corrosion generated. PP type coatings and H, generated similar value of potential corrosion. By comparing this value with substrate, a protective effect against degradation phenomena of the coatings was observed. Density and corrosion rate were decreased substantially by applying the protective film, the corrosion rate was decreases by five orders of magnitude. As a result of exposing the specimens to salt spray for 2000 hours, there was an increase in density and corrosion rate in all tested cases, being most pronounced for the substrate. However, it still maintains the protective effect of the coatings corroborating these results with the values obtained for the corrosion potentials.

The formation of the impedance spectra in the Nyquist plot for both the PP probe, and for the H1 and H2, are graphed consisting of two semicircles (fig 4). These systems are represented by an equivalent circuit shown in Figure 7.

The equivalent circuit of Figure 7, is applicable to coatings exposed to salt chamber in 0 hours and 2000 hours. The difference is set to the magnitude of the polarization resistance values (Rct). The parameter Rs represents the resistance of the electrolyte; in this case the

evaluation in saline (NaCl) acidified which corresponds to the resistance between the working electrode and reference electrode. In case of PP and H coatings, its magnitude was small, it is in the order of 1×10^5 Ω. Cc is the capacitance of the coating layer and R_{po} is the resistance of the solution-coating interface. In the case of base paint systems, refers to coating conformed by the system of the primer epoxy Alodine 5700 and topcoat, and in the case of system H refers to the system formed by Alodine 5700, antacid resin primer and Hetron197-3 , where the increase in Cc is consistent with a measure of the level of coating degradation.
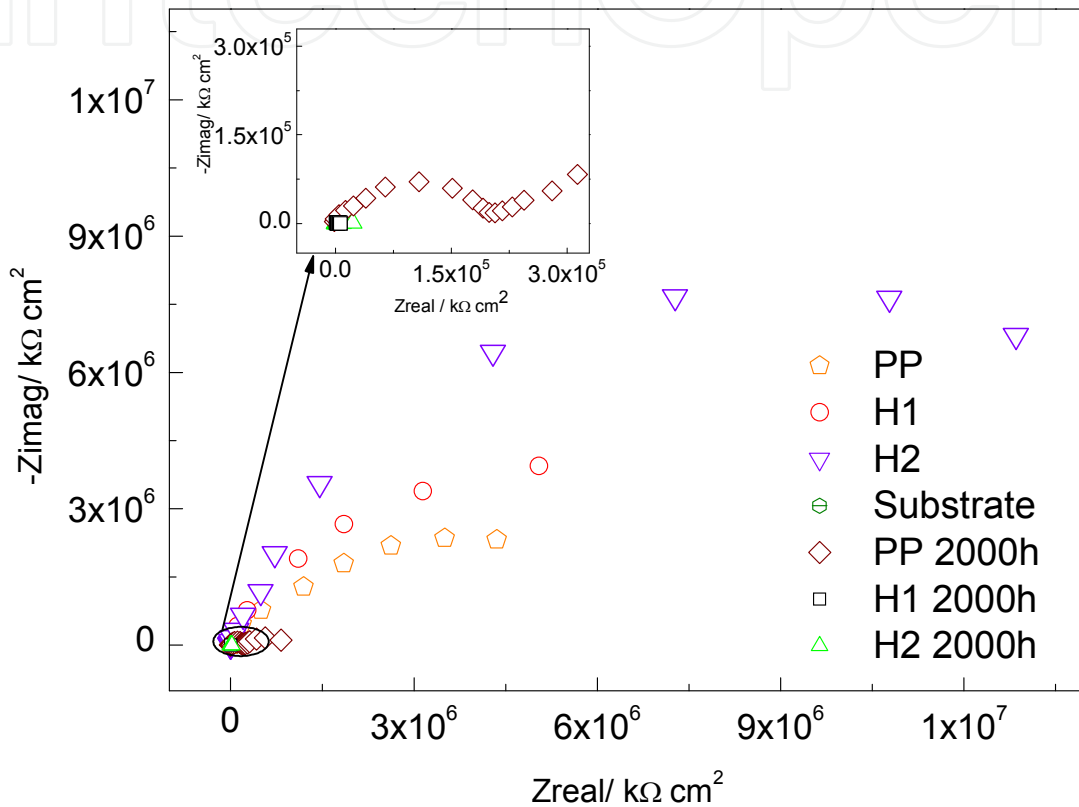

Figure 6. Nyquist plots of the substrate and coating types PP and H, evaluated in the salt chamber at 0 hours and 2000.

The decreasing in R_{po} is corresponding with increasing of water absorption or permeability thereof. Differentiate the contribution of each of the layers to the total resistance to corrosion may be performed by EIS, it follows that the first semicircle the Nyquist plots corresponding to the resistive contribution of the organic coatings (epoxy primer and synthetic resins), because the input resistive the conversion coating is relatively small compared to the organic coatings and therefore it is not clearly recorded in the input impedance in the system of corrosion protection. At 0 hours of exposure, the R_{po} value of the H coating with 1 and 2 layers is close to 1×10^9 Ω and the PP coating exhibits 1×10^8 Ω for the PP, however after 2000 hours of exposure, the R_{po} of the H and PP coatings decreased to 1×10^6 Ω, also the value of PP is higher. This indicates that the permeability is increased dramatically in the H coating compared to the PP coating, and is also reflected in the decrease in polarization resistance and corrosion kinetics because when the coating is permeated, the ionic species

are reaching the coating-substrate interface and reduced the polarization resistance and increased the corrosion rate, this behavior is similar to that found in the Tafel polarization curves. The Cdl is the capacitance of the double layer while its increase is an indicator of coating adhesion loss (Osborne, 2001). The Rct represents the resistance to the charge transfer (polarization resistance) associated with the kinetics of the corrosion process. This parameter is inversely proportional to the corrosion rate and the oxidation occurrence area (Reynolds, 1997). Therefore, coating systems have a good performance as a corrosion protection system with respect to the substrate, due to high Rpo and Rct values and low values of Cc and Cdl for 0 hours to 2000 hours of exposure in the mist chamber.
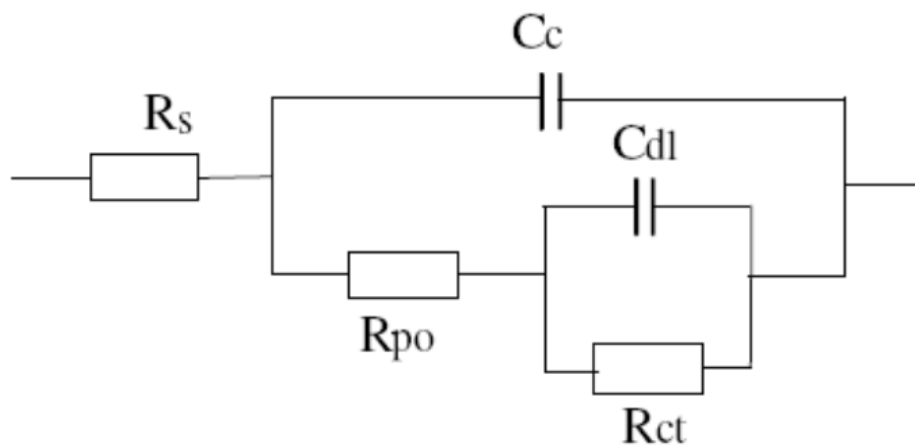

Figure 7. Equivalent circuit diagrams used to explain Nyquist coatings for H1, H2 and PP.

3. Conclusions

According to the Tafel polarization curves and Nyquist plots, the coatings of polyester antacid resin has the lowest value of current and rate corrosion with the traditionally system used in the aviation industry without exposure to mist chamber.

After 2000 hours of mist chamber exposure, the system of the PP has a smaller decrease in the corrosion current comparing to H system, which is due to the higher moisture permeability of the polyester resin.

The effect of thickness on the coating base polyester antacid resin is not significant (corrosion rates of H1 and H2 are 0.817 and 0.608 respectively) as to the results of corrosion rate when there is an increased thickness around 100 μm, passing from one layer (1 layer) to 200 μm (2 layers) approximately.

Characterization techniques by SEM confirmed that after 2000 hours of exposure in saline acidified chamber, the adhesion and coating substrate interface, in the systems of the PP and H haven't visible deterioration.

Synthetic resin based coatings can be used in areas not subjected to impact, unless they are reinforced with glass fiber fabrics, which potencialice impact resistance and coating integrity guarantee and the mechanism of protection by chemical barrier.

The mist chamber during 2000 hours of operation, was under the conditions laid down by ASTM B117, with respect to the variables of temperature in the exhibition area, condensate collection, relative humidity and thus the reliability of results.

The coating AH1 presents an added value in terms of their relative low cost and readily available in the market, therefore, is of great interest to continue the use of such configurations in synthetic resin coatings.

Author details

Willian Aperador Chaparro
Ingeniería Mecatrónica, Universidad Militar Nueva Granada, Bogotá, Colombia

Acknowledgement

4. References

Airframe, Hanbook. *Airframe & Powerplant Mechanics* (1999), U.S Departament of transportation, Federal Aviation Administration.

Aperador, W., Vera, E. and Vargas, A. (2010) "Estudio de la resistencia a la corrosión electroquímica de electro-recubrimientos níquel/cobre obtenidos por corriente pulsante" Ingeniería & Desarrollo. Universidad del Norte. 27(2): 48-61.

ASM, Hanbook. *Metallography and Microstructures.* (2005). ASM international the materials information society.

ASTM B 117 – 09 (2008). Standard, Standard Practice for Operating Salt Spray (Fog) Apparatus, West Conshohocken, PA, American Society for Testing and Materials.

ASTM B 209 – 07 (2007) Standard, Standard Specification for Aluminum and Aluminum-Alloy Sheet and Plate, West Conshohocken, PA, American Society for Testing and Materials.

Atta, A, M. and Elsaeed, A,M. (2006). "New Vinyl Ester Resins Based on Rosin for Coating Applications". Reactive & Functional Polymers, 66(6): 1596–1608.

Atta, A, M. and Nassar, I.F. (2007). "Unsaturated polyester resins based on rosin maleic anhydride adduct as corrosion protections of steel" Reactive & Functional Polymers, 67(4): 617–626.

Atta, A,M. and Elsaeed, A,M. (2007). "Unsaturated Polyester Resins Based on Rosin Maleic Anhydride Adduct as Corrosion Protections of Steel". Reactive & Functional Polymers, 67(3): 549–563

Bierwagen,G.P. and Tallman, D.E. (2001) "Choice and measurement of crucial aircraft coatings system properties" Progress in Organic Coatings, 41(2): 201–216.

Buchheit, R.G. and Guan,H. (2003). "Active corrosion protection and corrosion sensing in chromate-free organic coatings" Progress in Organic Coatings, 47(4): 174–182.

ESTCP, reporte de. *Non-Chromate Aluminium Pretratments*. (2004). Environmental Security Techology Certification Program.

Groover M.P, Pearson Prentice Hall. 1997.Dr H, Lijain, "Aircraft corrosion, Agard - Corrosion protection schemes for aircraft structures: some examples for the corrosion behavior of al-alloys"; Germany.

Munger C. G, Corrosion Prevention by Protective Coatings, NACE; Houston, Texas, 1984, cap. 3, 4, 5.

Neuder, H. and Sizemore, C. "Chrome-Free Single-Step In-Situ Phosphatizing Coatings on a Ti-6A1-4V Titanium Alloy" Progress in organic coatings, 47(3): 307 -311.

Oñate, A. E. *Las Aeronaves y sus Materiales. Tecnología Aeronáutica*. (1991). Madrid, España, Paraninfo. ISBN: 0-89100-058-5.

Osborne, J. H. (2001). "Inorganic/organic hybrid coatings for aircraft aluminum alloy substrates" Progress in Organic Coatings, 41(4): 217-225.

Reynolds, L.B. and Twite, R. (1997). "Preliminary evaluation of the anticorrosive properties of aircraft coatings by electrochemical methods" Progress in Organic Coatings, 32(3): 31-34.

Sanchez-Amaya, J.M. and Osuna, R.M. (2007). "Monitoring the degradation of a high solids epoxy coating by means of EIS and EN" Progress in Organic Coatings, 60 (4): 248–254.

Sathiyanarayanan, S., and AZIM, S. (2008). "A new corrosion protection coating with polyaniline–TiO2 composite for steel" Electrochimica Acta, 53(6): 2087–2094.

Twite, R.L. and Bierwagen, G. P. (1998) "Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys", Progress in organic coatings, 33(2): 91-100.