



# Non-Destructive Evaluation of Protective Coatings on AA2024-T3 Aluminum Alloy Used in Aeronautical Parts by Electrochemical Impedance Spectroscopy

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**Abstract:** The 2xxx aluminum alloys are largely used in aeronautical structural applications (fuselage, wings) due to their high mechanical strength/weight ratio, but have poor localized corrosion resistance. Their anticorrosive protection is generally ensured by multi-layered coatings based on inorganic and organic layers. The usual technique to evaluate the corrosion protection efficiency provided by the coatings is the salt spray test (ASTM B117). Nevertheless, though the test is employed worldwide, it presents some weak points, such as: it is a destructive test, subjectivity of test (only visual evaluation by the operator), low correlation between conditions of the test and real conditions, low reproductibility. The electrochemical impedance spectroscopy would be an alternative: non-destructive test, objectivity of the test (impedance measurement), the test can be performed in-situ.

In this work, uncoated and coated AA2024-T3 alloys were tested in solutions of NaCl 3.5wt% at room temperature. The coatings were: (a): chromating conversion coating; (b): (a) + epoxy primer; (c): (b) + top coat; (d): chromic anodizing coating; (e): (d) + epoxy primer; (f): (e) + top coat. The specimens of AA 2024-T3 divided into seven groups of duplicates (each group representing a superficial state, non protected or a type of coating) were submitted to electrochemical impedance spectroscopy at corrosion potential using frequencies in the 0.1 to 100 kHz range. To ensure reliability of the results, a design of experiment based on a saturated factorial design was applied involving two control variables (treatment of surface and alternating current frequency), one response variable (impedance modulus) and two blocks (samples and repetitions). Some simulations of surface degradation via standardized accelerated tests (salt spray test) and simulations of common defects in process or assembly operations in aircraft manufacture according to valid standards in the aeronautical industry were also made on coated AA2024-T3 specimens. These surfaces were also tested using electrochemical impedance spectroscopy under the same experimental conditions (3.5 wt% NaCl, room temperature, 0.1Hz-100kHz). The statistical analysis of results showed the effectiveness of the application of electrochemical impedance spectroscopy to assist in the quality control of processes of surface treatments in the aerospace sector. The synergic effect involving the care taken in the experimental conditions, the type of experimental design and the sampling size were important to validate the results facing violations of hypotheses in the analysis of variance method. Each coating on AA2024-T3 alloy, and also the bare metal, is characterized by an Impedance versus Frequency Bode curve, sort of fingerprint, which can be used to identify the coating and to evaluate easily and accurately its quality. The results have demonstrated promising and allow to establish strategies for implementation of the electrochemical impedance spectroscopy technique in surface treatment processes.

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## INTRODUCTION

The 2xxx series alloys are heat-treatable aluminum-copper alloys which present high mechanical strength due precipitation hardening and good fatigue resistance. Due to their high mechanical strength/weight ratio, they are largely used in aerospace and aircraft structural applications.

Nevertheless, these alloys have poor localized corrosion resistance due to copper that tends to precipitate at grain boundaries, turning these copper rich regions more cathodic than the surrounding aluminium matrix that will act as anode or preferential site for corrosion through galvanic coupling. This makes the metal very susceptible to pitting, intergranular corrosion and stress corrosion cracking. The alloy of 2xxx series that will be used in this study is AA2024-T3 that contains 3.8 to 4.9 % Cu and was solution heat-treated, cold-worked and naturally aged. Its use has been already reported

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in the fabrication of wings of the DC-3 in 1935, but it is also nowadays used in fuselages and tails [1].

The anticorrosive protection of the 2xxx aluminum alloys is generally ensured by multi-layered coatings based on inorganic and organic layers. Chromating chemical conversion [2, 3] and anodizing [2, 4] coatings are usually employed in aeronautical industry as the inorganic layers on the bare metal. The first one is mainly composed of hydrated Cr<sub>2</sub>O<sub>3</sub> oxide and presents self-healing. The layer has low electrical resistivity and provides corrosion resistance to parts which must present electrical conductivity such as electrical bonds in aeroplanes. Anodizing leads to the formation of an Al<sub>2</sub>O<sub>3</sub> oxide layer. Chromic anodizing is used when it is difficult to remove the residual electrolyte. Sulphuric anodizing must not be employed in this case. The layers obtained by the latter process have excellent corrosion resistance and can be colored. Both chromating conversion and anodizing layers are also used as a base for painting [5]. The organic coating is constituted of two layers: primer and top-coat. The role of the primer is to bond to the surface, inhibit corrosion, and provide an anchor point for the finish. Epoxy primer which will be used in this work is a synthetic, thermosetting resin that produces tough, hard and chemical-resistant coating [6]. But other primer types can be used in the aircraft setor: wash primers, red oxide primer, gray enamel, urethane. Among the finish coating (synthetic enamel, lacquers, polyurethane, urethane, acrylic urethane), polyurethane is preferred in aviation industry for abrasion-, stain-, and chemical-resistance and high degree of resistance to damage from UV rays from the sun [7].

The usual technique to evaluate the efficiency of the corrosion protection provided by the coatings is the salt spray test (ASTM B117) [8]. Nevertheless, though the test is employed worldwide since several decades (the first version of the standard dates 1939), it presents some weak points, such as: it is a destructive test, subjectivity of test (only visual evaluation by the operator), low correlation between

conditions of the test and real conditions, low reproducibility. Certainly, it is still in use because corrosion-test requirements in the salt spray test are contained in many industry specifications and there is no other accelerated corrosion test to replace this universal test. Alternate accelerated corrosion tests were developed in the 90' and showed to reproduce better the real conditions. One of these tests is reported in SAE J2334 standard which was first edited in 1998 and was applied successfully in automotive industry.

The electrochemical impedance spectroscopy [9] would be an alternative test for the evaluation of the protective efficiency of coatings. It is a non-destructive test. Indeed, it consists to apply a small perturbation of potential (few millivolts) around the natural null-current potential of the specimen and to measure the response in current. The test is objective since the final measurement is impedance values. The test can be performed in-situ, because corrosion sensors have been developed, which can be permanently attached to the structure to be monitored, or to be hand-held and carried up to the structure.

In this work, AA2024-T3 alloy coated by chromating chemical conversion, chromic anodizing, epoxy primer and polyurethane finishing layers were tested in solutions of NaCl 3.5wt% at room temperature by electrochemical impedance spectroscopy. To assure reliability to the results, a design of experiment based on a saturated factorial design was applied. Some simulations of corrosion degradation and of common defects in aircraft manufacture were also made and electrochemical impedance spectroscopy was also applied for characterization.

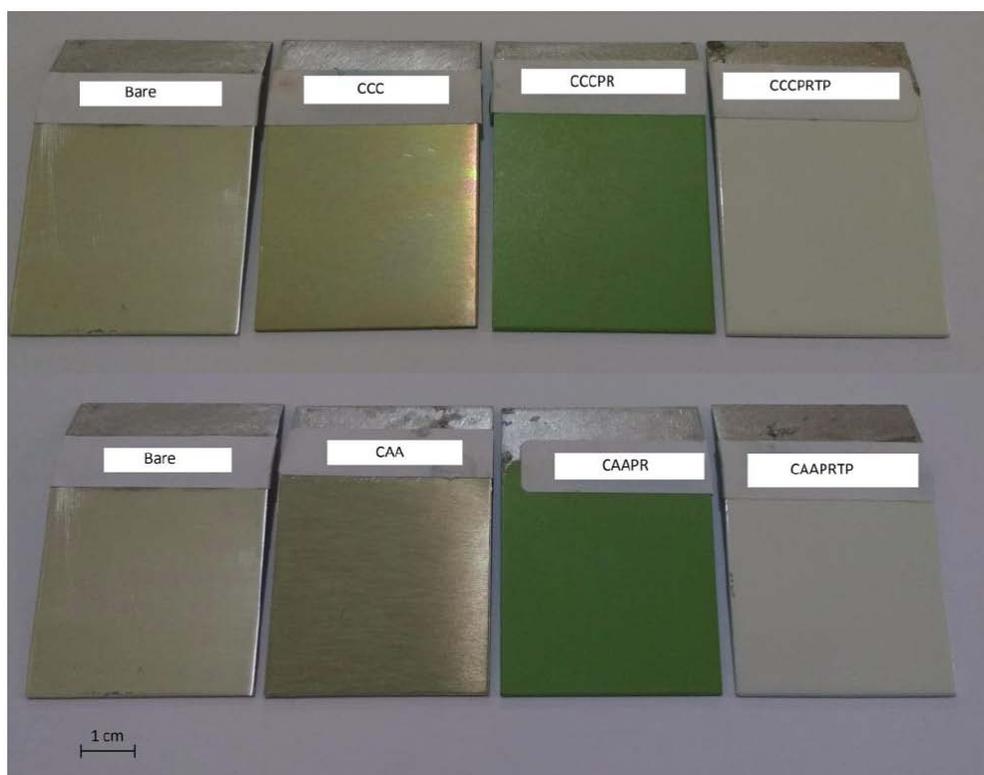
## EXPERIMENTAL PROCEDURE

### Materials

The aluminum alloy used was AA2024 alloy whose composition is: 90.7-94.7 Al; 0.1 max Cr; 3.8-4.9 Cu; 0.5 max

**Table 1: Coatings Applied on the AA2024-T3 Alloy and their Respective Codes**

Code	Surface Treatment
Bare	No surface treatment
CCC	Chromating chemical conversion (Alodine 1200S™) according MIL-C-554 [3]
CCCPR	Chromating chemical conversion (Alodine 1200S™) according MIL-C-554 [3] + Epoxy primer (green) according to MIL-PRF-23377 [6]
CCCPRTP	Chromating chemical conversion (Alodine 1200S™) according MIL-C-554 [3] + Epoxy primer (green) according to MIL-PRF-23377 [6] + Polyurethane top coat (white) according to MIL-PRF-85285 [7]
CAA	Chromic anodizing according to MIL-A-8625 [4]
CAAPR	Chromic anodizing according to MIL-A-8625 [4] + Epoxy primer (green) according to MIL-PRF-23377 [6]
CAAPRTP	Chromic anodizing according to MIL-A-8625 [4] + Epoxy primer (green) according to MIL-PRF-23377 [6] + Polyurethane top coat (white) according to MIL-PRF-85285 [7]



**Figure 1:** Surface treatments on AA2024-T3 alloy listed in Table 1.

Fe; 1.2-1.8 Mg; 0.3-0.9 Mn; 0.5 max Si; 0.15 max Ti; 0.25 max Zn; 0.05 max other, each; 0.15 other, total (wt%). The AA2024 alloy was under the T3 condition (heat-treated, cold-worked and naturally aged).

The bare metal (without coating) and six types of coatings were tested (Table 1).

The uncoated and coated coupons were rectangular in shape (4 cm x 6 cm) and had 0.1 cm thickness. Figure 1 presents the surface of the different types of coupons. The electrical contact during impedance tests was made on an uncoated part on the top of the coupon (Figure 1). The CCC, CAA, PR and TP layers are nearly 9, 2, 57 and 52 micrometers thick, respectively.

### EIS Experiments

The EIS experiments were performed in 3.5 wt% NaCl solution at room temperature. The solution was naturally aerated and the experiments were operated without stirring. A flat cell was employed using a square-shaped platinum sheet of 18 cm<sup>2</sup> area as counter-electrode and a saturated calomel electrode (SCE) as reference electrode. Prior to EIS tests, the working electrode (bare metal or coated sample (Figure 1)) was immersed in the solution for 1 h, then the impedance measurements were performed at open-circuit potential using a sinusoidal signal of 10 mV amplitude and frequencies in the range of 0.1 Hz to 100 kHz (61 frequency values). The Electrochemical Interface SOLARTRON model 1287A and the Frequency Response Analyzer SOLARTRON

model 1260 A, controlled by the Ecorr/Zplot SOLARTRON model 125587S software, were used.

### DOE and Statistical Analysis

Two samples originated of the same batch (bare, CCC, CAA, CCCPR...) were tested and five EIS experiments were performed on different regions of each sample.

The DOE used in this study can be represented by a randomized block design with two factors (frequency – real and continuous factor, and type of surface treatment – categorical and non-quantitative factor) or by a saturated factorial design with four factors (frequency, type of surface treatment, samples (two per treatment) and repetitions (five per sample)) [10]. The response variable was the modulus of impedance. The design was the matrix array shown in Figure 2.

The statistical analysis of the impedance data was based on variance analysis and was made using Statgraphics Centurion XV software. It was expected to evaluate the repeatability and reproducibility of impedance curves, to distinguish accurately the impedance curve for each surface treatment and to detect any discrepancy.

Some simulations of corrosion degradation via standardized accelerated tests (salt spray test) and simulations of common defects in process or assembly operations in aircraft manufacture according to valid standards in the aeronautical industry were also made on coated AA2024-T3 specimens.

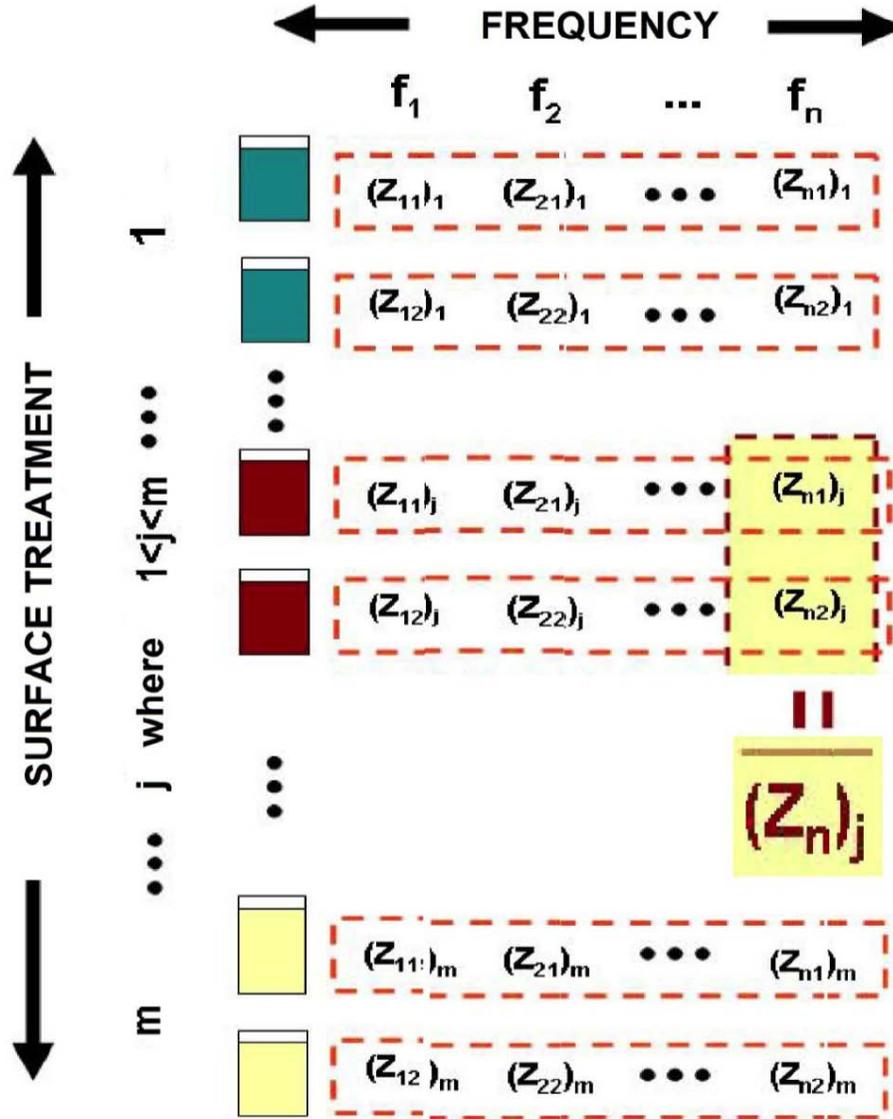


Figure 2: Matrix array used for EIS experiments on uncoated and coated AA2024-T3 alloy.

EIS tests under these conditions were made in the same way and the results were compared with the “standard” impedance curves.

## RESULTS AND DISCUSSION

### Statistical Analysis

All impedance results sum a total of 4270 values. It was only considered the influence of the pure factors i.e. frequency, surface treatment, sample and repetition, and the interactions of first order (interactions between two main factors). The interactions of higher orders were used as mean square deviation. Table 2 shows the analysis of variance (ANOVA) [10] obtained from these results.

In ANOVA, P value is the probability value which gives the degree of confidence at which the factor (or interaction) is significant. The P values in Table 2 indicate that almost all

single variables and first order interactions were significant in the response variable (impedance modulus), except AD interaction (frequency x repetitions) and CD interaction (sample x repetitions). However, the Mean Square column that provides how expressive the variable or interaction influences the impedance modulus response, shows that only variable B (Surface Treatment) and variable A (frequency) really influence impedance response. The other factors and interactions are significant but have low significance in the impedance modulus.

As impedance modulus only depends on surface treatment and frequency, a Bode graph ( $Z$  vs  $f$ ) was drawn for each surface treatment (Figure 3). Each curve is the average of the values obtained on two samples with five repetitions each. The dispersion of values was adjusted to a confidence interval of 95% in a  $\pm 0.4$  logarithmic unit around the average value.

Table 2: ANOVA of Impedance Modulus Response

Variability Sources	Sum of Squares	Degrees of Freedom	Mean of Squares	F <sub>Snedecor</sub>	P Value
FACTORS					
A: Log <sub>10</sub> (Frequency, Hz)	5570,46	60	92,841	4656,74	0,0000
B: Surface Treatment	11087,6	6	1847,94	92689,14	0,0000
C: Sample	29,1289	1	29,1289	1461,05	0,0000
D: Repetitions	0,343266	4	0,0858166	4,30	0,0018
INTERACTIONS					
AB	265,174	360	0,736594	36,95	0,0000
AC	5,74741	60	0,0957902	4,80	0,0000
AD	3,26552	240	0,0136063	0,68	0,9999
BC	124,66	6	20,7766	1042,12	0,0000
BD	1,36432	24	0,0568466	2,85	0,0000
CD	0,175695	4	0,0439237	2,20	0,0662
Residual	69,8589	3504	0,0199369		
Total	17157,8	4269			

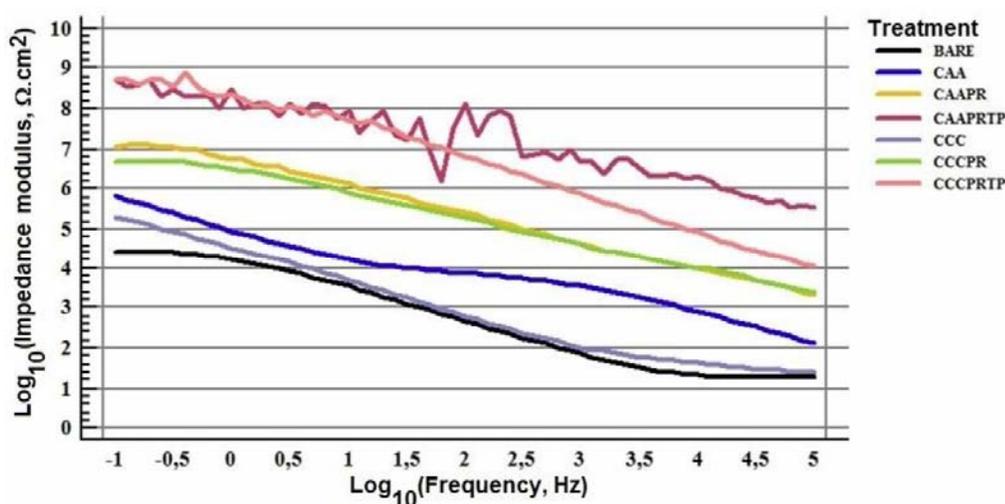


Figure 3: Impedance modulus versus frequency Bode graphs as a function of surface treatment (95% interval of confidence).

The curve representative of a given surface treatment is a sort of fingerprint, which can be used to identify the coating and to evaluate easily and accurately its quality.

Having all the information regarding impedance response with 95% accuracy for each surface treatment, it was possible to create a hierarchy graph for each type of surface treatment, based on the average impedance over the whole frequency range (Figure 4). Uncoated AA2024T3 alloy (“bare” condition) and CCC condition (Chromating chemical conversion) have similar response in impedance and show the lowest mean impedance values, i.e. present the lowest corrosion resistance. CAA layer provides better corrosion resistance than CCC layer. In all cases, coatings which contain CCC underlayer are always less corrosion resistant than coatings that contain CAA under layer (Figures 3 and 4).

### Simulations of Surface Degradation

#### Salt-Spray Test

CCC samples were submitted to the Salt spray test (ASTM B117) up to 120 hours and after different exposure times, EIS test was applied. The corresponding Bode graphs (impedance modulus versus frequency) are shown in Figure 5 as a function of exposure time. The decrease in impedance modulus at low frequencies with the exposure time clearly indicates a decrease in corrosion resistance of the coated alloy with aging in chloride medium (quantitative evaluation). Although the visual observation of the sample surface (qualitative evaluation) is the worldwide method, it did not allow detecting any change in the coating quality in our case, whereas EIS clearly indicates a decrease in corrosion resistance.

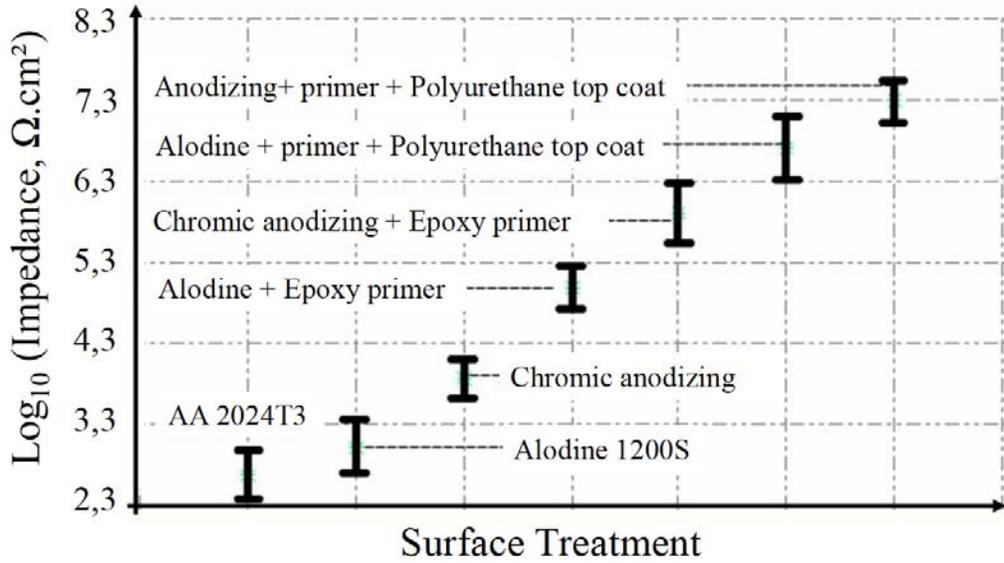


Figure 4: Mean impedance for each surface treatment over the whole frequency range (interval of confidence 95 %).

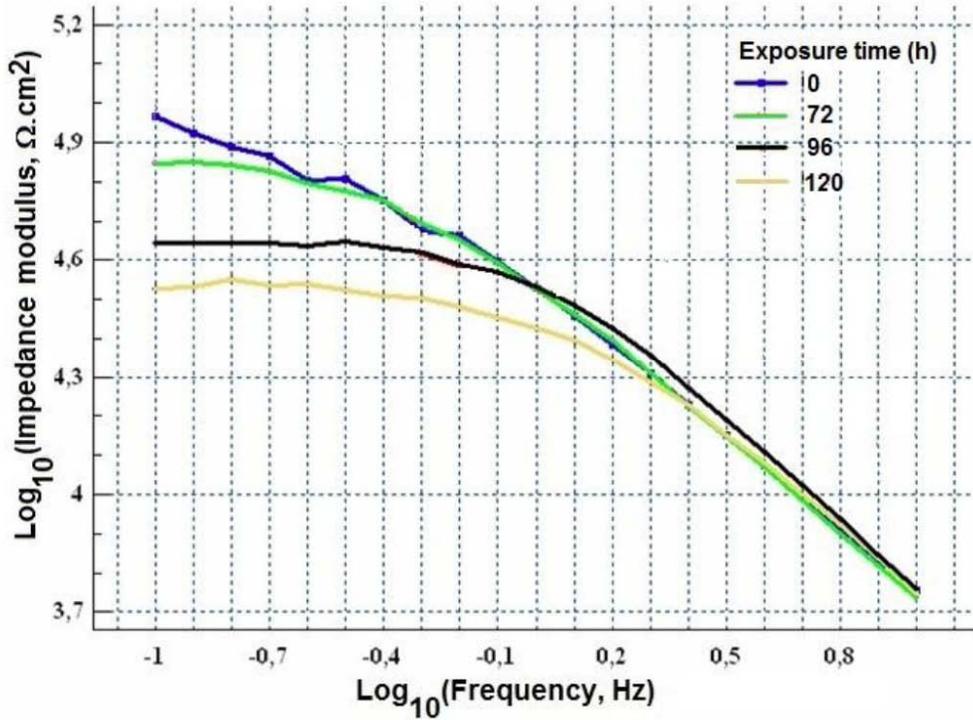


Figure 5: Impedance modulus versus frequency Bode graphs of CCC samples as a function of exposure time to salt spray test.

**Thermal Degradation of CCC Coating**

Figure 6 shows impedance modulus versus frequency Bode graphs of CCC samples after drying at 60 and 90°C in air. It is clearly evidenced that there is a loss in corrosion resistance due to temperature exposure. It was shown [11] that exposure from ambient to low temperature (<150°C) leads to dehydration, cracking of the chromate conversion coating, immobilization of Cr (VI) species, avoiding self-healing. EIS shows to be a valuable technique to detect any mistake of process.

**Simulations of Common Defects during Assembly Operations of Aeronautical Components**

Surface damage of different severity levels was performed on CCCPRTP samples using some common tools (Figure 7). It can be seen from Figure 8 that impedance modulus versus frequency Bode graphs of surface with hole and slight scratch are very similar to that of not damaged CCCPRTP. This evidences that such defects are not detrimental to the performance of the coating. Moderate and deep scratches that allow reaching the base metal decrease the corrosion resistance. Indeed, it is noted a clear decrease in impedance

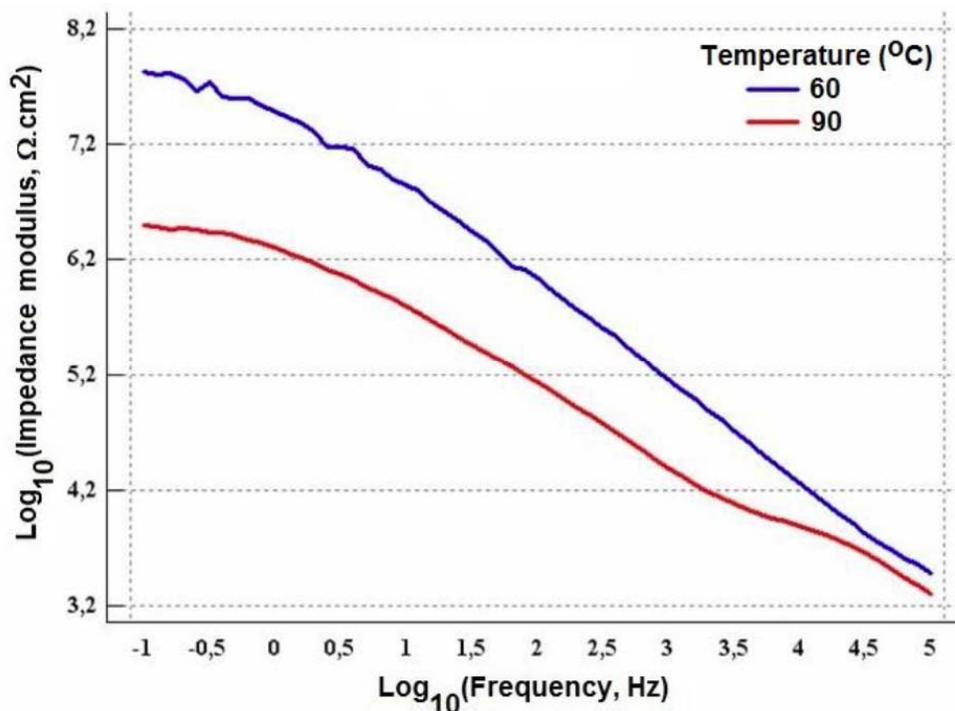


Figure 6: Impedance modulus versus frequency Bode graphs of CCC samples after drying at 60 and 90°C before painting with epoxy primer.

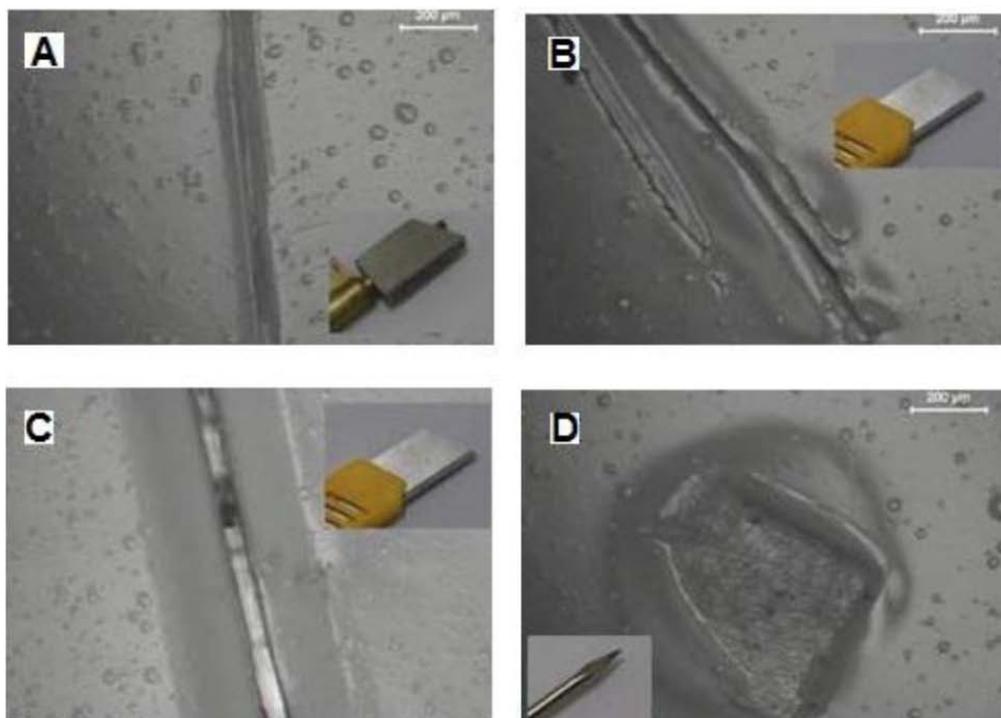


Figure 7: Surface damage performed on CCCPRTP samples using some common tools: (A) slight scratch; (B) moderate scratch; (C) deep scratch; (D) hole.

modulus at low frequencies. Nevertheless, the impedance values do not reach the values of the AA2024-T3 alloy (bare) due the anti-corrosive pigments contained in the polymeric layers and the active protection provided by the chromating chemical conversion underlayer.

## CONCLUSIONS

Common protective coatings on AA2024-T3 aluminum alloy used in aeronautical parts were evaluated by electrochemical impedance spectroscopy in 3.5 wt% NaCl solution at room

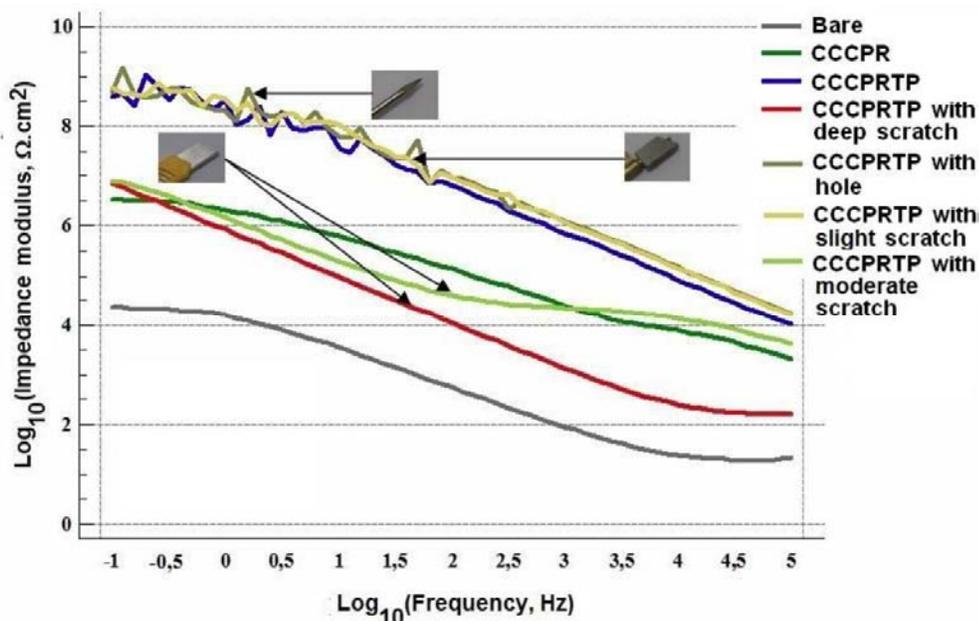


Figure 8: Impedance modulus versus frequency Bode graphs of CCCPRTP samples after surface damage according Figure 7.

temperature: (a): chromating conversion coating; (b): (a) + epoxy primer; (c): (b) + top coat; (d): chromic anodizing coating; (e): (d) + epoxy primer; (f): (e) + top coat.

Each coating on AA2024-T3 alloy, and also the bare metal, is characterized by an Impedance versus frequency Bode curve, sort of fingerprint, which can be used to identify the coating and to evaluate easily and accurately its quality with 95% of interval of confidence.

Aging of coatings (by salt spray exposure for example), mistake in the coating process (drying temperature of chromating conversion coating before painting with epoxy primer higher than the standard temperature in this work) or surface damage during assembly operations can be easily detected via electrochemical impedance spectroscopy measurements.

## REFERENCES

[1] ASM Handbook Volume 2, Properties and selection: Non-ferrous alloys and special-purpose materials. ASM International 1990.

- [2] ASM Handbook Volume 5, Surface Engineering. ASM International 1994.
- [3] Military Standard. MIL-C-5541: Chemical Conversion Coatings on Aluminum and Aluminum Alloys.
- [4] Military Standard. MIL-A-8625: Anodic Coatings for Aluminum and Aluminum Alloys.
- [5] Forsgren A. Corrosion Control Through Organic Coatings. CRC Press 2006.
- [6] Military Standard. MIL-PRF-23377: Primer Coatings: Epoxy, High-Solids.
- [7] Military Standard. MIL-PRF-85285: Coating: Polyurethane, Aircraft and Support Equipment.
- [8] Baboian R. Corrosion Tests And Standards: Application and Interpretation. 2nd ed. ASTM International 2005.
- [9] Lasia A. Electrochemical Impedance Spectroscopy and its Applications. New York: Springer-Verlag 2014.
- [10] Cox DR, Reid N. The Theory of the Design of Experiments. Chapman and Hall/CRC 2000.
- [11] Laget V, Isaacs HS, Jeffcoate CS, Buchheit RG. Dehydration-induced loss of corrosion protection properties in chromate conversion coatings on aluminum alloy 2024-T3. J Electrochem Soc 2003; 150: B425-32.