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Abstract: In this work some organic natural products were studied, namely tannic acid, gallic acid, mimosa tannin and chestnut tannin, as potential green corrosion inhibitors of the aluminium alloy AA2024-T3. The anodizing treatment was performed in a solution of the referred organic compounds in diluted sulfuric acid. The electrochemical impedance spectroscopy and the potentiodynamic polarization were performed to assess sealing quality and corrosion protection granted by the anodic films. To understand the green inhibitors; interaction with the metal surface, FTIR spectra of anodizing and anodizing and sealed samples of AA2023-T3 were recorded, and the shifts in the position of the major bands confirmed that the green inhibitor interacts with the metal surface. Images of the morphology of the coatings were provided by Scanning Electron Microscopy. From the results obtained through the various techniques that were used to carry out this study it is possible to conclude that the formed anodic films can be a good contribution for the prevention of corrosion in the aluminium alloy AA2024-T3.

Keywords: green corrosion inhibitors; tannins; aerospace industry; anodization; aluminium alloys

1. Introduction

Aluminium alloy AA2024-T3 is usually used in the aeronautical industry due to its high strength and good mechanical properties. The composition of this alloy shows that Cu (4.4%), Mg (1.5%) and Mn (0.6%) are present, as well as minor amounts of Fe and Si. Due to the presence of these intermetallic particles, the aluminium's resistance to corrosion is limited and corrosion protection is needed [1–20].

The anodising process in acidic media, mainly in sulfuric, chromic, boric or phosphoric acids, is widely used in the aeronautical industry to protect the aluminium alloys. On the other hand, former conversion treatments based on hexavalent chromium compounds have been restricted because these compounds are carcinogenic and have high environmental toxicity [12,13,20,21].

Anodic films obtained by anodizing in acid media usually consist of two layers, the inner one being a thin compact layer (100–150 Å) located next to the metal (barrier layer) [22], the thickness of which is directly proportional to the applied potential. The porous outer layer material, resulting from the etching of the acid to the oxide formed during anodizing process, consists of hexagonal columnar cells with a cylindrical pore at the center of each cell. These cells may reach up to about 100 μ m thick under certain experimental conditions. To increase the corrosion resistance of these films, the pores of the oxide film must be blocked, which is achieved via immersion of the alloy in boiling water (sealing process). A hydrated oxide layer (bohemite, Al₂O₃·H₂O) is thus formed, closing the pores [22].



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The pores of the anodic film formed in sulfuric acid solution without any other chemical added are not well defined and the distribution is irregular [19]. In the literature several alternatives are described for better organizing the porous layer thus formed based on the use of anodising baths composed of mixtures of inorganic acids such as boric/sulfuric acid or by mixtures of organic/inorganic acids, such as the tartaric acid-sulfuric acid anodising bath (TSA) used by AIRBUS company [15]. The pores of the anodic films formed in TSA are well distributed and appear to be well organized [19].

The oxide film formed by anodization in the TSA bath does not dissolve in this medium but tartaric acid can combine with aluminium cations to produce aluminium tartrate. If the conversion coating is exposed to a corrosive environment, aluminium tartrate, despite its low solubility in water, may re-dissolve in some extension, producing a local buffer and thereby limiting the susceptibility to localized corrosion [15,22].

The inhibition of metal corrosion using green inhibitors in acidic media is a subject under development and a great number of studies are available. Usually, these inhibitors are organic compounds that contain heteroatoms such as O, N or S and sometimes multiple bonds, which may allow their chemical adsorption on the metal surface [23–32]. These studies are focused on the use of naturally occurring substances in order to find low-cost and non-hazardous inhibitors [27]. Examples of organic inhibitors include carboxylic acids, alkaloids, polyphenols and various plant extracts [33–35].

Tannins comprise a wide range of natural biodegradable polyphenols [31–39]. They have been used since antiquity to tan animal skins to form leather [29]. They are macro-molecules with a molecular weight between 500 and 30,000 Da. Tannins are divided into two major groups, the hydrolysable tannins and the condensed tannins [30,37,40,41], and two less important ones, the phlorotannins and the complex tannins (Figure 1).



Figure 1. Tannin classification.

The hydrolysable tannins are esters of a monosaccharide, usually glucose, and phenolcarboxylic acids, and can be divided into two sub classes: gallotannins and ellagitannins. The condensed tannins are polymeric derivatives of flavonoids [34]. From acidic hydrolysis, gallotannins produce gallic acid and ellagitannins produce ellagic acid. Hydrolysable tannins such as chestnut bark and sumac leaves, the last one being a source of tannic acid, are used in the tanning industry. In gallotannins, the hydroxyl functions (OH) of the monosaccharide core can be partly or completely esterified with galloyl units. This class of compounds is present in many plants with important biological properties. Tannic acid, the most representative compound of this class, is constituted by a glucose central unit whose



hydroxyl groups are esterified with digalloyl units linked by a meta-depside bond [40,41], Figure 2.

Figure 2. Chemical structure of tannic acid with the digalloyl ester sub-unit marked.

Ellagitannins also contain a monosaccharide esterified with gallic acid and at least one hexahydroxydiphenoyl residue formed by oxidative coupling between two galloyl units. Investigation of the constitution of chestnut tannin, an ellagitannin, indicated that the main components are monomeric vescalagin and castalagin, which represent 40–60% of this ellagitannin, Figure 3 [41].



Figure 3. Chemical structure of castalagin ($R_1 = H, R_2 = OH$) and vescalagin ($R_1 = OH, R_2 = H$).

The condensed tannins, also known as proanthocyanidins, are oligomeric or polymeric flavonoids, and are based on flavan 3-ol units linked via a carbon-carbon bond, Figure 4A. These tannins are found in the bark of several trees, such as mimosa and quebracho [40]. Mimosa tannin is mainly a trimer of three flavan-3-ol units with a catechin/gallocatechin (R' = H/R' = OH) basic structure, Figure 4B [41].



Figure 4. Chemical structure of the main polyphenol (A) and trimer compound (B) of mimosa tannin.

Complex tannins are formed from an ellagic acid unit and a flavan-3-ol unit linked to a monosaccharide unit and are rare. Phlorotannins are present in brown seaweeds and are polyphenolic compounds formed by polymerization of phloroglucinol units.

The literature describes the corrosion inhibition effect of tannins for steel alloys and carbon steel [30,36,39] resulting from the adsorption of these compounds on a metal surface and the blocking of active surface sites, thus reducing the corrosion rate [27]. The same authors describe the four types of adsorptions that may take place by these organic molecules at the metal/solution interface:

- (a) electrostatic attraction between the organic molecules and the metal;
- (b) interaction of oxygen lone electron pairs with the metal;
- (c) interaction of tannin molecule π -electrons with the metal;
- (d) combination of (a) and (c).

The stability of the corrosion inhibitor film on the metal surface depends on some physicochemical characteristics of the organic molecule, such as its functional groups, aromaticity, possible steric effects and electronic density of heteroatoms, which may act as electron donors. The type of corrosive medium, the structure and the charge of the metal surface and the nature of the interaction between the π -orbital of inhibitors with the d-orbital of metal are also very important to the stability of the inhibitor film [27].

The efficiency of corrosion inhibition by organic compounds can be related to the amount of adsorbed organic inhibitor on the metal surface. The adsorption of a corrosion inhibitor is possible due to the residual charge on the surface of the metal and the nature and chemical structure of the organic compound. On a metal surface, the inhibitor is bonded by physical or electrostatic forces and chemisorption [28,30]. When adsorption occurs due to electrostatic forces, since these forces are weak, the reverse process will also occur easily. Indeed, organic charged species do not make direct contact with the metal due to the presence of a layer of water molecules that separates them [30].

Interaction between polar organic species and metal surfaces can occur by another process, chemisorption. This process is slower than electrostatic sorption and is temperaturedependent. It shows higher inhibition efficiencies at higher temperatures. Chemisorption of the organic compounds can be performed through the existence of polar functional groups or groups that can dissociate [30].

Tannins have been used as corrosion inhibitors for iron and steel, as mentioned previously. They can form chelates with metallic cations due to the presence of vicinal hydroxyl groups on aromatic rings. Tannins also have been referred to as rust converters since their presence converts active rust into non-reactive protecting oxides. Protection properties result from the reactions of polyphenolic sub-unit of the tannin molecule with ferric ions, thereby forming highly cross-linked network metallic-tannates [27–39]. Other studies [42] have elucidated the inhibitory actions of chestnut tannin on metal corrosion by means of the frontier orbital theory. These authors using the results of the molecular modelling and corrosion rate measurements found that tannin constituents probably adsorb as neutral species by means of electrostatic forces that act between the molecular dipoles and the charged metal surface.

Martinez et al. [43–45] studied the corrosion of steel in the presence of mimosa tannin or gallic acid and, using molecular modelling, showed that adsorption of tannin molecules could proceed via sharing of the non-bonding electrons of the -OH group of the polyphenol aromatic subunit, with the partially filled d-orbitals of a metal, e.g., iron.

The literature describes how mimosa tannin reacts with Fe³⁺ produced at anodic sites to form ferric tannate species [46,47]. Ross et al. [48] suggested that the structure of the ferric tannate chelate obtained with mimosa tannin contains three tannate ions, each tannin ion coordinating two vicinal hydroxyl group to the metallic ion, thus forming a stable octahedral coordination compound.

Due to the large number of vicinal phenolic hydroxyls, each molecule could react with a few metallic ions to form a network structure [30,36,46], Figure 5.





Since there are a limited number of papers reporting the prevention of the corrosion of aluminium alloys by natural corrosion inhibitors, the purpose of this study was to clarify the interaction of some commercial tannins with the AA2024-T3 aluminium alloy. Tannic acid,

chestnut bark and mimosa tannin were selected. The first two are hydrolysable tannins, the former a gallotannin and the second one an ellagitannin. Mimosa tannin is a condensed one. Gallic acid present in all of those tannins as a galloyl residue was also investigated. To achieve this goal, the surface of the treated alloy was tested by polarization assays and electrochemical impedance spectroscopy, and FTIR spectra of the metallic samples were recorded to investigate the presence of the organic inhibitor at the metal surface. The long-term stability of the baths used in the anodizing of AA2024-T3 was also investigated by UV-Vis spectroscopy.

2. Materials and Methods

2.1. Sample Preparation

The reagents used were gallic acid (p.a.) provided by Alfa Aesar, Thermo Fisher (Kandel) GmbH, Germany, tannic acid, (p.a.) provided by Riedel-de-Haen, Honeywell Research Chemicals (Laborspirit, Loures, Portugal) and the mimosa and chestnut tannins provided by CTIC (Centro Tecnológico das Indústrias do Couro, Alcanena, Portugal). The inhibitor solution (electrolyte solution) was prepared by dissolving the tannin (5 g/L) in H_2SO_4 (0.46 M).

Corrosion tests have been carried out on AA2024-T3 aluminium alloy samples. The aluminium alloy 2024-T3 has a nominal composition (wt/wt) of 0.05% Si, 0.11% Fe, 4.4% Cu, 0.55% Mn, 1.4% Mg, 0.01% Cr, 0.02% Zn, 0.02% Ti, 0.01% V, 0.04% other elements and the remainder in Al.

AA2024-T3 aluminium alloy was cut into specimens with dimensions of $50 \times 15 \times 0.6$ mm. The samples were degreased by washing first in acetone and then in deionized water, mechanically sanded using successively finer grades of SiC papers (N° 400, N° 800, N° 1200 and N° 1500) and finally rinsed with deionized water.

Before anodising, the samples were dished in a commercial chromate-free alkaline cleaner (Turco 4215 NCLT-HENKEL) at 65 °C for 15 min. Finally, they were dipped in a chromate-free commercial acid etching bath (SOCOSURF 1858) at room temperature for 5 min. After each step they were rinsed in distilled water. Then, an anodizing area of 6 cm² was delimited using Teflon tape. The anodization was performed using a Peak Tech DC Dual Power Supply 6010D, using a lead sheet with an area of 32 cm² as cathode, by applying a potential difference of 14V for 25 min at a temperature of 35 °C. After the anodization procedure, the specimens were washed in distilled water at room temperature and then the specimens were subjected to the sealing process that consisted in immersion in a distilled water bath at 96 °C for 20 min. Next, they were dried and kept in a desiccator.

2.2. UV-Vis Spectra

UV-Vis spectra of anodizing baths were acquired on Shimadzu 1603 double beam spectrophotometer (Izasa Scientific, Lisboa, Portugal) using 1 cm quartz cells. Spectra of the solution containing the organic inhibitor $(0.01 \text{ g} \cdot \text{dm}^{-3})$ in H₂SO₄ (0.46 M) was recorded over 12 months after its preparation.

To determine the stability of the anodizing bath over time, the initial UV-VIS spectra of each bath was recorded before any experiment. The samples were diluted with H_2SO_4 (0.46 M) until the inhibitor reached a concentration of 0.007 g·dm⁻³.

2.3. Electrochemical Measurements

The EIS measurements were carried out using a CH Instruments electrochemical analyser CHI604D and all the measurements were performed at room temperature in a Faraday cage. A three-electrode arrangement was used in a conventional electrochemical glass cell. A saturated calomel electrode (SCE, 0.241 V vs. NHE) was used as reference and a large area platinum coil employed as counter electrode, the probed area of the working electrode (6 cm²) being restricted using a teflon tape.

The electrolytic medium consisted of a 0.5M NaCl aqueous solution naturally aerated. MILLI-Q water (18.2 M Ω ·cm at 25 °C) was used to prepare the test solutions. Prior to any

electrochemical experiment, the open-circuit potential of the specimen was continuously monitored for 50 min. It was found that this period of the time was enough to reach a stable potential plateau with an oscillation of less than 1mV in the last 5 min of OCP monitoring.

The EIS data were obtained over the frequency range 10^{-1} – 10^{5} Hz with 12 points per decade, using a 3 mV (rms) sinusoidal potential perturbation [20]. The resulting spectra were fitted using CHI Electrochemical Software version 1.0.0.1.

The potentiodynamic polarization experiments were carried out at a scan rate of 0.2 mV/s, starting from -200 mV below the open circuit potential (OCP) and finished not prior to the pitting potential having been reached, the measurements being repeated in duplicate. The corrosion current (I_{corr}) was obtained from the intercept of extrapolated cathodic and anodic Tafel lines at the corrosion potential (E_{corr}).

2.4. FTIR Spectroscopy

FTIR analyses were carried out using a Nicolet 6700 spectrometer (ThermoUnicam, Miraflores, Portugal) equipped with a Smart SAGA[™] (Specular Apertured Grazing Angle) Accessory. Spectra were recorded in the 4000–400 cm⁻¹ range with a resolution of 4 cm⁻¹, averaging 128 scans per sample. The data were collected with Omnic 3.1 software.

2.5. Scanning Electron Microscopy (SEM)

The surface morphology of the samples anodized and anodized and sealed was evaluated by Scanning Electron Microscopy (SEM) using a Hitachi S2400 equipment. The samples were deposited with Au/Pd before the SEM analysis.

3. Results and Discussion

3.1. Morphology Analysis

Changes in the surface of aluminium samples anodized in sulfuric acid baths containing the organic compounds under study, namely gallic acid (GSA), chestnut tannin (CSA), mimosa tannin (MSA) and tannic acid (TNSA), and sealed after anodization were investigated by SEM (Figure 6).

The above figures show that the anodized and sealed samples are more homogeneous when compared to the samples only anodized. After sealing, the samples show some areas with a crystalline appearance and the extension of these areas are greater in the sample treated in the TNSA bath. This type of morphology has already been reported by other authors in similar studies [24]. The sample anodized and sealed in the CSA bath is the one that exhibits a compact and homogeneous surface, which results in a better anticorrosive performance, as described below. According to literature [19,24,26,49], when samples are treated in a bath composed only with sulfuric acid (SA bath), they present pores not well defined and with an irregular distribution, which points to the better performance of the CSA bath when comparing it to the SA bath.

3.2. Coating Characterization

FTIR spectra of all samples were recorded and are depicted in Figure 7 and Tables 1 and 2. The interpretation of these results led to the conclusion that, after the anodizing process, all samples present a similar spectrum in the region of 1400 to 400 cm⁻¹ (Figure 7A), thus leading to the further conclusion that the appearance of bands in this region of the spectrum is due to the anodization process and consequently are not related to the presence of the organic corrosion inhibitors on the surface. A similar record was obtained from samples subjected to anodizing, followed by the sealing processes (Figure 7B). The spectra of anodized samples show different bands in the region 4000–1400 cm⁻¹, which can be explained by the presence of different organic inhibitor molecules inside the pore. After the sealing process, FTIR of samples treated in baths containing the organic corrosion inhibitor present new bands in this range when compared to the FTIR spectra of the sample treated with a bath containing only sulfuric acid (SA). These new bands are probably related to the formation of complexes with the metallic ions Al³⁺ and Cu²⁺ formed during the

anodization process. After the sealing process it is possible to observe the decrease of the band at 980 cm^{-1} and the appearance of a new band at approximately 500 cm^{-1} in all spectra.



Figure 6. Illustrative SEM photomicrographs of the AA2024-T3 (A1) anodized in CSA bath, (A2) anodized in CSA bath and sealed, (B1) anodized in GSA bath, (B2) anodized in GSA bath and sealed, (C1) anodized in MSA bath, (C2) anodized in MSA bath and sealed, (D1) anodized in TNSA bath and (D2) anodized in TNSA bath and sealed.



(B)

Figure 7. FTIR spectra of the samples (A) anodized and (B) anodized and sealed.

From the data presented in the above spectra and tables it is possible to conclude that the anodizing process was effective in all samples, since the band of adsorbed H₂O corresponding to the hydrated oxide layer appears at 4000–3000 cm⁻¹ in all spectra [50,51].

In the FTIR spectra of the anodized sample in the SA bath, the two bands at 3419 cm⁻¹ and 3037 cm⁻¹ are attributed to -OH bands and the band at 1635 cm⁻¹ may be attributed to H–O–H bands of hydration water of aluminium oxides. The band at 1151 cm⁻¹ corresponds to the Al–O–H bending, which is evidence of the presence of boehmite. The band at 980 cm⁻¹ is attributed to the stretching vibration of Al = O of alumina and confirms the presence of aluminium oxides and the band at 651 cm⁻¹ is attributed to v_{as} Al–O in the

octahedral oxide AlO₆. The difference observed in the spectra of anodized and anodized and sealed samples is related to the formation of boehmite in the sealing process, the appearance of a band at 501 cm⁻¹ being assigned in the literature to the Al–O bonds of boehmite [42,51-54].

Table 1. FTIR absorption maxima observed in spectra of porous aluminium oxide produced in a $0.46 \text{ M} \text{ H}_2\text{SO}_4$ solution containing the green inhibitor.

SA	GSA	TNSA	CSA	MSA	Assignments	References
		3815 vs	3990 vs	3963 vs	ν_{as} O-H	[40]
3414 vs 3037 vs	3400 vs 3062 vs	3531 vs	3446 vs	3427 vs	vO-H streching	[40,50,52]
1635 vs	1637 m			1624 s	$\nu O\text{-}H(H_2O)$ and $\nu_s COO^-$	[16,40]
		1552 s 1464 s	1577 s 1475 s	1543 s	$\nu_{as}COO^{-}$	[16,40]
		1132 m	1132 s	1134 m	ν C-O-C cyclic ether	[40,42,51–54]
980 s	980 s	980 s	980 s	980 s	$\nu_{as} \; AlO_4 \; and \; \delta AlO_4$	[40,42,51–54]
629 vw	633 vw	638 w	629 w	623 w	$v_{as} AlO_4$	[40,42,51–54]
561 s	560 w	559 w	561 w	530 w	$\nu_{as} AlO_6$	[40,42,51–54]

vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

Table 2. FTIR absorption maxima observed in spectra of porous aluminium oxide produced in a $0.46 \text{ M} \text{ H}_2\text{SO}_4$ solution containing the green inhibitor, after the sealing process.

SA	GSA	TNSA	CSA	MSA	Assignments	References
3984 vs	3813 vs		3826 vs	3840 vs	ν _{as} Ο-Η	[40]
		3695 vs			ν_s O-H	[40,51]
3325 vs	3495 vs 3174 vs	3537 vs 3089 vs	3485 vs	3477 vs 3190 vs	vO-H streching	[40,51]
1635 w	1635 m	1635 s	1633 w	1641 m	ν O-H (H ₂ O) and ν_{s} COO ⁻ [16,40]	
1151 m		1144 m	1140 m	1138 m	ν C-O-C cyclic ether	[40,51–55]
	1051 w	1059 vw	1078 vw	1057 w	β = C-H deformation	[40,51–55]
947 w	903 w	908 w	918 w	916 w	$\nu_{as} \mbox{ AlO}_4$ and $\delta \mbox{AlO}_4$	[40,51–55]
654 vw	650 vw			665 w	$\nu_{as} AlO_4$	[40,51–55]
501 s		513 vw	511 w	519 w	$\nu_{as} AlO_6$	[40,51–55]
	476 s	476 s	478 w	476 s	δAlO ₄	[40,51–55]

vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

In the anodizing baths, tannin molecules can coordinate two or more OH groups with aluminium and/or copper cations. The presence of aluminium and/or copper produces a difference in the vCOO⁻ vibrations of this tannin functional group. For the anodized sample in GSA bath, a band at 1637 cm⁻¹ is attributed to v_sCOO^{-} . After the sealing process, a new band appears at 1402 cm⁻¹ and an increase of the band at 1637 cm⁻¹ is observed. This is probable due to the formation of complexes between gallic acid and Al cations. After the sealing process, the spectra present a strong band at 3062 cm⁻¹ corresponding to the vOH. The bands at 3485 cm⁻¹ correspond to the vOH of adsorbed H₂O [55].

In the spectra of the sample treated in TNSA it is possible to identify the νCOO^- at 1552 and 1464 cm⁻¹. The bands at 2540, 2854, 2924 and 2947 cm⁻¹ correspond to the νC -H vibration and at the band 3500 cm⁻¹ can be attributed to the νO -H. After the sealing process, it is possible to observe the displacement of the bands corresponding to νCOO^- . These significant changes in spectra profile of TNSA treated sample at the range 1700–1400 cm⁻¹

are due to the chelation products formed between the tannin and the cations during the electrochemical process [54,55]. In addition, FTIR spectra of samples treated with TNSA inhibitor present distinguished bands in 3089 cm⁻¹ and 3537 cm⁻¹, attributed to vOH of adsorbed H₂O and, at 3695 cm⁻¹, to vOH belonging to the Al–OH bond.

The spectrum of the anodized sample in MSA shows a band at 2675 cm⁻¹ due to the vC–H vibrations and two strong bands at 3427 cm⁻¹ and 3963 cm⁻¹, corresponding to the vOH vibration in the Al–OH group. After the sealing process, the band at 1543 cm⁻¹ disappears and the band at 1624 cm⁻¹ decreases. Mimosa tannin is formed by catechin units linked together. Of the various compounds studied, it is the only one that has a 1,2-dihydroxybenzene catechol ring in its constitution, which is easily oxidized to an o-quinone so that it can be hypothesized that the appearance of a new band at 1867cm⁻¹ in the FTIR spectrum may correspond to vibrations vC=O of a complex that will form between the aluminum and/or copper ions and the carbonyl groups of the o-quinone residue.

The spectra of anodized samples in the CSA bath present two strong bands at 1475 cm^{-1} and 1577 cm^{-1} . These bands correspond to strong and asymmetric vibration of aromatic C=C and a complex carboxylic group, respectively. These bands disappear after the sealing process. In the spectra of anodized and anodized and sealed samples in the CSA bath, the bands corresponding to vOH are present at 3485 cm⁻¹ and 3826 cm⁻¹.

In the spectra of anodized samples prepared with the TNSA, MSA and CSA baths, it is possible to observe a weak band around 2800 cm⁻¹ that, according to the literature [49], can be attributed to strong intramolecular hydrogen bonds in organic compounds.

3.3. Stability of the Bath Solution

The stability of the bath solution to be used in the anodizing process was monitored over 12 months using UV spectroscopy. To study the bath stability over time the UV spectra of the bath solutions were recorded between 200 and 400 nm. Figure 8 shows the overlapped spectra for all studied baths. Regarding the GSA bath, it can be seen that all spectra present two bands with $\lambda_{max1} = 214$ nm and $\lambda_{max2} = 272$ nm and two inflection points at 202 nm and 239 nm. The results obtained led us to affirm that the solution is stable during this period of time. The TNSA bath spectra profile is similar to the GSA bath spectra. These spectra also show two intense bands with $\lambda_{max1} = 213$ nm and $\lambda_{max2} = 274$ nm and two inflection points at 202 nm and 241 nm. The slight increase in the intensity of the bands can be due to a small evaporation of the solvent during a year which resulted in a higher concentration of the tannin. MSA bath spectra show that this tannin solution is also stable over time, with $\lambda_{max} = 280$ m and an inflection point at 258 nm. The CSA bath spectra show a flattening in the region 240–260 nm after 2 months, indicating some instability over time probably due to decomposition/hydrolysis of some constituents.

Spectra presented in Figure 9 were obtained with freshly prepared solutions and after these solutions were used in more than twenty anodization experiments. From this figure it is possible to verify that only the MSA solution presents a strong alteration, which may be due to the consumption or, more likely, to the electrochemically oxidation of tannin molecules promoted during the anodizing process. TNSA solution spectra, before and after the twenty anodizing experiments, also present a slight difference, which can be due to the hydrolysis of tannic acid and the formation of free gallic acid in the bath, in accordance with the small wavelength shift observed in bands. Spectra of the other two solutions involved in the study only reveal a minor decrease of the signal amplitude resulting from the consumption of the organic compounds. For the GSA bath the two spectra have λ_{max} at the same value, 214 and 272 nm, and for the CSA bath the wavelength values of maximum absorbance and shoulder have almost the same value, which is an indication that these baths are not degraded by the anodizing process.



Figure 8. UV spectrum of the (A) GSA, (B) TNSA, (C) CSA and (D) MSA solutions over 12 months.



Figure 9. UV spectrum of the (**A**) GSA, (**B**) TNSA, (**C**) CSA and (**D**) MSA solutions before and after anodized process.

3.4. Electrochemical Measurements

The behavior of the anodizing and sealed samples regarding corrosion was also studied by EIS. The spectra are presented in Figures 10–14. The physical transformations that occur in the porous layer formed during the anodizing process on the surface of the samples are reflected in the variations of impedance that occur at high and medium frequencies [15–19]. Analyzing the results, it is possible to conclude that the anodized specimen in TNSA solution presents a smaller variation in impedance value (|Z|) with immersion time, when compared to the samples anodized in other corrosion inhibition media involved in this study. From the analysis of the spectra, it is also possible to conclude that the anodized specimen in the GSA solution presents the more susceptible barrier layer to corrosion when compared to the other samples, which can be confirmed by the decrease of the impedance value (|Z|). At the same time, slight shifts of phase-angle were observed during the immersion time. This behavior may be due to the increase in the corrosion phenomenon promoted by the contact with the corrosive agents. The analysis of these spectra also allows us to conclude that the samples anodized in the TNSA, CSA and MSA baths have better barrier properties than the GSA and SA baths.



Figure 10. Bode plots for AA2024-T3 anodized at 35 °C in SA and sealed for prolonged immersion in NaCl 0.5 M. (**A**) Bode modulus and (**B**) Bode phase.



Figure 11. Bode plots for AA2024-T3 anodized at 35 ·C in CSA and sealed for prolonged immersion in NaCl 0.5 M. (**A**) Bode modulus and (**B**) Bode phase.



Figure 12. Bode plots for AA2024-T3 anodized at 35 °C in GSA and sealed for prolong immersion in NaCl 0.5 M. (**A**) Bode modulus and (**B**) Bode phase.



Figure 13. Bode plots for AA2024-T3 anodized at 35 °C in TNSA and sealed for prolonged immersion in NaCl 0.5 M. (**A**) Bode modulus and (**B**) Bode phase.



Figure 14. Bode plots for AA2024-T3 anodized at 35 °C in MSA and sealed for prolonged immersion in NaCl 0.5 M. (**A**) Bode modulus and (**B**) Bode phase.

Different equivalent circuits have been proposed to fit the behavior of porous anodic films. Figure 15A illustrate the physical description of the electric circuit used to describe the physical meaning of various electrochemical fit parameters. This model was successfully applied to explain the properties of the barrier and porous layer by Suay et al. [53]. The R_{sol} represents the resistance of the electrolyte, R_H and C_H correspond, respectively, to the resistance and capacitance of the surface layer of hydrated oxide, R_p is the pore resistance and explains the limitation of electrolytic charge transfer through pores and coating defects,

 C_p represents the capacitance of the formed pores and R_b and C_b parameters represent, respectively, the resistance and the capacitance of the barrier layer. The barrier effect of the hydrated oxide layer formed is very important in the corrosion protection of aluminium alloys, since it is the last layer that separates the electrolyte from the alloy. The entrance of the electrolyte into this barrier layer can cause its degradation, thus causing the corrosion of the alloy. The resistance and capacitance of the pore wall are represented by R_{pw} and C_{pw} , respectively.





(B)

(A)

Figure 15. Physical representation of the equivalent circuit used for interpretation of impedance data: **(A)** general model; **(B)** simplified model for sealed anodic used for fitting impedance data.

Figure 15B shows the physical model used by several authors [56–60] for fitting sealed anodic film. In this model, the R_{pw} and C_{pw} are both generally omitted since they are, respectively, extremely high and extremely low [57–60]. This model barely permits the conduction of ions through taking into consideration the infinitesimal current across the very large resistance [60–63]. However, from Bode plots, it can be said that the porous layer and barrier layer have heterogeneities, making their capacitive behavior better simulated by a constant phase element [56–60]. Therefore, the C_p and C_b represent the constant phase elements (CPE) corresponding to the non-ideal capacitance at the porous layer and the barrier layer. CPE is defined: CPE = $1/(j2\pi fC)^n$ [57–60].

The parameters n_p and n_b are influenced by CPE_p and CPE_b , respectively, due to the non-ideal capacitive behaviors. Parameter n is the frequency dispersion factor and varies from 1 to 0. When n = 1, CPE can be considered as real capacitances, whereas n = 0 represents a real resistance [58].

The results obtained from the fitting experiments are present in Figure 16. A representative example of fitting for the equivalent circuit indicated in the Figure 15B is included in Figures 10 and 11.

From the analysis of the results obtained for the R_p parameter presented in Figure 16A it is possible to verify that, at the beginning of immersion, the samples treated with baths containing the organic inhibitors present a higher pore resistance value when compared with samples treated in the SA bath. The sample treated in the TNSA bath is the one that presents a lower value when compared with the samples treated in baths with the other organic inhibitors. After a day of immersion in NaCl 0.5M solution, it was found that virtually all samples treated in CSA and MSA baths have a very sharp decrease, which means that the films begin to degrade. Opposite behavior was showed for samples treated in the TNSA, GSA and SA baths where this parameter increased. This behavior may be due

to the fact that the corrosion phenomenon is still very localized, since the corrosive solution can only reach the substrate through some paths that are formed as a consequence of the defects of the anodic film. Precipitation of corrosion products may then occur in these areas blocking the conductive pores [61]. Therefore, these paths are prevented and the resistance of the coating increases. It can also be speculated that, inside the pores, the green corrosion inhibitor can re-dissolve, producing a buffer solution which prevents local change in pH, thus limiting the localized corrosion. Such a phenomenon would be similar to what was reported for tartaric acid in a sulfuric acid bath: the residual tartaric acid can combine with aluminium cations during the conversion process to produce aluminium tartrate due to re-dissolution during the immersion in corrosive media, limiting the susceptibility to localized corrosion [15]. After 28 days, it was found that the samples present a close value for R_p parameter.



Figure 16. Variation of the values of (A) R_p , (B) CPE_p , (C) R_p and (D) CPE_b obtained from fitting.

Regarding the results obtained for the CPE_p parameter, Figure 16B, initially this value was very low for all samples; however, a slight increase was observed over the immersion time for the samples treated in the GSA and SA baths. The samples treated in the MSA, TNSA and CSA baths have a practically constant value over immersion time, which means that these samples are less permeable to an electrolyte rich in chloride.

From the results obtained for the parameters that allow evaluation of the properties of the barrier layer, the parameters R_b and CPE_b , we can conclude that the presence of the organic inhibitors in the baths promote better barrier properties.

In relation to the parameter R_b , it was possible to verify that, after 28 days, the sample treated in the GSA bath showed a R_b value close to the one of the sample treated with the SA bath, but lower when compared to the samples treated in baths containing the other

organic inhibitors, which means that this sample exhibited a worse barrier resistance when compared to the others samples.

Concerning the CPE_b parameter, it was observed that, initially, this parameter presented very low values for all samples. After 28 days, the sample treated in the SA bath showed a higher CPE_b in relation to the other samples treated in the other baths. From the results obtained it is possible to conclude that the GSA bath exhibited the worst performance, which probably is related to the fact that gallic acid molecules contain an inferior number of oxygen atoms than others organic inhibitors able to establish the interaction with the metal surface. This explanation also was mentioned in literature studies which evaluated the performance of corrosion inhibition on mild steel in HCl acid solution by tannic acid and gallic acid [62].

The values of n_p and n_b are presented in Table 3. The n_p behavior indicates that the porous layer is more resistant in the initial stage. In the beginning, the n_p value is close to 1, indicating that the barrier layer is relatively homogeneous and few defects are present. During the immersion time the number of defects increase and consequently the n_p and n_b decrease [58].

Table 3. Fitting results for EIS data for parameter n_p and n_b acquired in 0.5 M NaCl solution on different anodized and sealed samples.

	Days	SA	GSA	TNSA	CSA	MSA
	0	1.00	0.95	1.00	1.00	1.00
	1	0.82	0.57	0.88	0.81	0.85
n	3	0.77	0.41	0.84	0.72	0.85
пр	8	0.83	0.72	0.80	0.88	0.85
	16	0.79	0.51	0.75	0.84	0.72
	28	1.00	0.40	0.99	0.86	0.87
	0	0.86	0.87	0.91	0.91	0.91
	1	0.86	0.92	0.83	0.87	0.86
n	3	0.85	1.00	0.84	0.91	0.86
п _b	8	0.88	0.92	0.80	1.00	0.86
	16	0.77	0.88	0.74	0.97	0.88
	28	0.85	0.85	0.87	0.89	0.89

From the EIS results obtained it is possible to conclude that the presence of tannins in baths' conversion increases corrosion resistance and can therefore be a viable and sustainable alternative

The potentiodynamic polarisation plots for specimens in 0.5 M NaCl are shown in Figure 17 and the corrosion potential (E_{corr}) and corrosion current (I_{corr}) obtained for the bare and treated AA2024-T3 samples are summarized in Table 4. The results allow for the conclusion that the protection is effective for all samples treated, leading to a corrosion current (I_{corr}) decrease. Anodization followed by sealing in the SA, MSA and CSA baths produce anodic films that present I_{corr} values of the same order of magnitude. When anodization followed by sealing is performed in the TNSA and GSA baths, the same I_{corr} value of $\approx 5.0 \times 10^{-8}$ A/cm² is observed. It is also verified that aluminium samples AA2024-T3 treated in the CSA bath have a more negative corrosion potential ($E_{corr} \approx -0.706$ V vs. SCE) than the samples treated with the other organic inhibitor solutions.

As is well known, chloride can cause severe pitting in aluminium alloys. The difference between E_{corr} and E_{pit} , (ΔE) suggests a susceptibility to localized pitting corrosion. Furthermore, the more positive E_{pit} is relative to E_{corr} , the more resilient the sample is to pitting [63]. From the results obtained, it is possible to conclude that the CSA present a higher difference between E_{corr} (-0.706 V vs. SCE) and E_{pit} (\approx -0.691 V vs. SCE). For the others samples a significant perturbation was observed in the anodic branch of the log i vs. E plot, and the values of E_{corr} and E_{pit} presented the same value.



Figure 17. Polarization curves in 0.5M NaCl recorded at a scanning rate of 0.2 mV/s, starting from -200 mV below the open circuit potential, sweeping in the positive direction and finished not prior to the pitting potential being reached.

	E _{corr} (V vs. SCE)	I _{corr} (A/cm ²)
SA	-0.556 ± 0.003	$2.0~\pm~0.8 imes 10^{-9}$

 -0.582 ± 0.002

 -0.552 ± 0.004

 -0.706 ± 0.006

 -0.594 ± 0.006

Table 4. Summary of the electrochemical parameters measured for different specimens.

The TNSA sample showed a pitting potential (E_{pit}), ($E_{pit} \approx -0.552$ V vs. SCE), higher
when compared with the other samples involved in the study. The CSA sample present a
lower E _{pit} .

The results obtained permit us to conclude that the sample treated in the CSA bath show the lowest susceptibility to corrosion.

4. Conclusions

GSA

TNSA

CSA

MSA

The tannin compounds involved in this study present the general requirements to be employed as inhibitors of aluminium corrosion since they have the capacity to promote a passive/protective layer on its surface. Tannin molecules have several hydroxyl and carbonyl groups that contain oxygen atom with the ability to donate their lone pair of electrons in an interaction with the metal. Tannin molecules also have several aromatic π -bonds that provide the electrons needed to interact with the metal surface. Since they are large molecules, they also have the abilit to cover a large area of the metal surface with a firmly attached compact film, which is nontoxic to humans and the environment.

The use of FTIR spectroscopy showed two new bands at $1543-1577 \text{ cm}^{-1}$ and $1132-1134 \text{ cm}^{-1}$ corresponding to the stretching of carboxilate and cyclic ether bonds, respectively, indicating that tannins were absorbed on the surface of the metal, thereby protecting it from further corrosion attack. The difference in FTIR spectra of aluminium samples treated in baths that contain these tannins when compared to samples treated in only sulfuric acid bath confirms the complexing of tannins with metal ions and allow the conclusion to be reached that the interaction between the metal and the inhibitors occurs by hydroxyl and carboxyl groups present in the organic molecule.

 $5.0~\pm~0.5\times 10^{-8}$

 $5.0\ \pm\ 0.0\times 10^{-8}$

 $1.3\ \pm\ 0.6\times 10^{-9}$

 $2.3\ \pm\ 0.9\times 10^{-9}$

From the above electrochemical results, it is possible to conclude that the CSA bath is a better corrosion inhibitor regarding the aluminium alloy AA2024-T3 compared to the other tannin baths and SA bath. This fact can be confirmed because the sample treated in the CSA bath showed a lower I_{corr} value $(1.3 \pm 0.6 \times 10^{-9} \text{ A/cm}^2)$. The EIS results suggest that tannin baths, when compared to the SA bath, present the capacity to promote a more compact oxide barrier layer, which is a very important event in corrosion protection of aluminium alloys, since it is this last layer that separates the electrolyte from the metal alloy.

Since tannic acid, chestnut and mimosa tannin are obtained from renewable vegetable sources, these tannins can be considered as green inhibitors of the corrosion of aluminium alloy.

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