

Alternative surface treatments without chromium content in aeronautical aluminium alloys

Tartaric sulphuric anodising

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ABSTRACT

Aluminium and its alloys are widely used in the aviation sector due to their lightweight and their high specific strength. They require surface treatments in order to improve their corrosion resistance, such as anodising which has traditionally carried out using a chromic acid bath.

Although chromium has been regularly used in industry for more than a century and its applications are many and varied, progressively restrictions and rigorous controls have been imposed because of environmental, toxicological and health concerns.

The objective of this thesis is to study the tartaric-sulphuric anodising, an alternative anodising process without hexavalent chromium. The tests were performed on three aluminium alloys AA2024-T3, AA7175-T7351 and AA6061-T6. It was analysed the thickness, the coating weight, the corrosion resistance and the loss of the absorption power achieved by the anodic film with excellent results.

Also, it was studied the compatibility of the anodic coating with various current post-treatments. It was tested three different sealings: with hot water, with potassium dichromate and with the chemical conversion coating Bonderite® M-CR 1200S Aero. On samples without sealing, it was applied an epoxy primer and a polyurethane topcoat in use by Airbus. It was demonstrated the compatibility of all of them with the anodic film, except in the case of the Bonderite® M-CR 1200S Aero on the AA2024-T3 that did not pass the corrosion test.

Finally, it was analysed the performance of a new non-chromate product for the acid etching process. The alternative product studied, as a substitute of the current bath with sodium dichromate, was the Bonderite® Smutgo NCB that achieved successful results.

Keywords

Aluminium alloys, TSA (Tartaric-Sulphuric Anodising), CAA (Chromic Acid Anodising), Anodising

RESUMO

O alumínio e as suas ligas são amplamente utilizadas no sector da aviação devido ao seu baixo peso específico e elevada resistência específica. Porém estes materiais necessitam de tratamentos de superfície, a fim de melhorar a sua resistência à corrosão, tais como a anodização, a qual tradicionalmente é realizada num banho de ácido crómico.

Apesar da utilização do cromo na indústria há mais de cem anos, com muitas e variadas aplicações, têm surgido progressivamente restrições e controlos rigorosos por causa de preocupações ambientais, toxicológicas e de saúde.

O objetivo desta tese é o estudo de um processo de anodização alternativo sem cromo hexavalente, a chamada anodização tartárica-sulfúrica. Os testes foram realizados em três ligas de alumínio AA2024-T3, AA7175-7351 e AA6061-T6. Foi analisada a espessura, o peso anódico, a resistência à corrosão e a perda do poder de absorção conseguida pela película anódica. Foram obtidos resultados muito promissores.

Também foi estudada a compatibilidade da película anódica com vários pós-tratamentos. Foram testados três tipos de colmatagem: em água quente; numa solução contendo dicromato de potássio e numa solução contendo o produto Bonderite® M-CR 1200S Aero. Em provetes cuja solução de colmatagem não foi aplicada foi aplicado o primário epóxi e a tinta de acabamento em uso pela companhia Airbus. Foi demonstrada a compatibilidade de todos eles, excepto no caso da colmatagem com a solução contendo produto Bonderite® M-CR 1200S Aero na liga de alumínio AA2024 o qual não passou no teste de corrosão.

Finalmente, analisa-se o desempenho de um novo produto sem cromatos para o processo de ataque químico antes do processo de anodização. O produto alternativo estudado, como um substituto do actual banho com dicromato de sódio, foi o Bonderite® Smutgo NCB que alcançou muito bons resultados.

Palavras-chave

Ligas de Alumínio, TSA (Anodização Tartárica-Sulfúrica), OAC (Oxidação Anódica Crómica), Anodização

TABLE OF CONTENTS

1. Introduction	1
1.1. Scope of the project	1
1.2. State of art	2
1.2.1. Chromium	2
1.2.2. REACH regulation.....	2
1.2.3. Chromates in the aircraft industry	3
1.2.4. Alternatives processes without chromates.....	4
2. Theoretical review	6
2.1. Aluminium and its alloys.....	6
2.1.1. Aluminium.....	6
2.1.2. Aluminium alloys.....	7
2.1.2.1. AA2024-T3.....	7
2.1.2.2. AA6061-T6.....	7
2.1.2.3. AA7175-T7351.....	8
2.2. Anodising process.....	8
2.2.1. Pre-treatments	9
2.2.1.1. Degreasing and cleaning.....	9
2.2.1.2. Etching	9
2.2.2. Anodising.....	10
2.2.2.1. Anodic film structure	11
2.2.2.1.1. Barrier anodic films.....	11
2.2.2.1.2. Porous anodic films	12
2.2.2.2. Electrolytes.....	12
2.2.2.2.1. Chromic acid electrolyte	13
2.2.2.2.2. Tartaric sulphuric electrolyte	14
3. Experimental procedure	17
3.1. Test specimen definition	17
3.1.1. Materials.....	17
3.1.2. Dimensions.....	18

3.2.	Test specimen preparation process	18
3.2.1.	Test specimen pre-treatments	20
3.2.1.1.	Alkaline pre-degreasing	20
3.2.1.2.	Alkaline degreasing	21
3.2.1.3.	Acid etching.....	21
3.2.2.	Test specimen anodising	23
3.2.2.1.	TSA anodising installation	23
3.2.2.2.	Bath manufacture.....	25
3.2.2.3.	Bath analysis	26
3.2.2.4.	Anodising process	29
3.2.3.	Test specimen post-treatments.....	30
3.2.3.1.	Sealing with hot demineralised water	30
3.2.3.2.	Sealing with Bonderite® M-CR 1200S Aero.....	30
3.2.3.3.	Sealing with potassium dichromate.....	31
3.2.3.4.	Paint.....	31
3.2.3.4.1.	Primer.....	31
3.2.3.4.2.	Topcoat.....	32
3.3.	Quality tests	32
3.3.1.	Coating thickness	32
3.3.1.1.	Scope	32
3.3.1.2.	Fundamentals.....	32
3.3.1.3.	Methodology.....	33
3.3.1.4.	Coating weight	34
3.3.1.5.	Scope	34
3.3.1.6.	Methodology.....	34
3.3.2.	Corrosion resistance	35
3.3.2.1.	Scope	35
3.3.2.2.	Fundamentals.....	35
3.3.2.3.	Methodology.....	35
3.3.3.	Paint adhesion	37

3.3.3.1.	Scope	37
3.3.3.2.	Methodology.....	37
3.3.3.2.1.	Dry adhesion test	37
3.3.3.2.2.	Wet adhesion test.....	38
3.3.4.	Dye spot test	39
3.3.4.1.	Scope	39
3.3.4.2.	Fundamentals.....	39
3.3.4.3.	Methodology.....	39
3.3.5.	Dye spot test with prior acid treatment.....	40
3.3.5.1.	Scope	40
3.3.5.2.	Fundamentals.....	40
3.3.5.3.	Methodology.....	40
4.	Results.....	41
4.1.	Quality of the TSA anodic film.....	41
4.1.1.	TSA coating thickness	42
4.1.2.	TSA coating weight	43
4.1.3.	TSA coating corrosion resistance.....	45
4.1.4.	TSA coating degree of sealing.....	47
4.2.	Quality of the post-treatments.....	49
4.2.1.	Post-treatments corrosion resistance.....	49
4.2.1.1.	Sealing with potassium dichromate.....	49
4.2.1.2.	Sealing with Bonderite® M-CR 1200S Aero.....	51
4.2.2.	Post-treatments dye spot resistance.....	55
4.2.2.1.	Sealing with potassium dichromate.....	55
4.2.3.	Paint adhesion	57
4.2.3.1.	Dry paint adhesion test	57
4.2.3.2.	Wet paint adhesion test.....	60
5.	Conclusions	63
6.	Bibliography.....	64

LIST OF FIGURES

Figure 1. Chromate applications in the aviation sector [5].....	4
Figure 2. Airbus A340 materials [wt.%] [9].....	6
Figure 3. Electrochemical cell.....	10
Figure 4. Anodic film structure: (A) Barrier anodic film, (B) Porous anodic film [10].....	11
Figure 5. Scanning electron micrograph of the porous anodic film [10].....	12
Figure 6. CAA electrolytic cycle [6].....	13
Figure 7. TSA electrolytic cycle [12].....	14
Figure 8. OGMA's facilities.....	17
Figure 9. TSA anodising process.....	19
Figure 10. Bonderite® Smutgo NCB bath.....	22
Figure 11. TSA anodising bath.....	24
Figure 12. Total acid titration.....	27
Figure 13. Sulphuric acid titration.....	28
Figure 14. TSA electrolytic cycle.....	29
Figure 15. Scheme of the eddy current generation on the test specimens.....	33
Figure 16. Coating thickness gauge, Elcometer 355.....	33
Figure 17. Salt spray chamber Ascott S1000t and NaCl solution tank.....	36
Figure 18. Supports of the spray salt chamber.....	36
Figure 19. Erichsen Multi Cross Cutter Model 295.....	37
Figure 20. Positioning of adhesive tape.....	38
Figure 21. Application of the Sanodal G on the samples: (I) Alloy 7175, (II) Alloy 2024 and (III) Alloy 6061.....	39
Figure 22. Sealing with hot water corrosion test: (a) Alloy 7175 etching with Bonderite® Smutgo NCB, (b) Alloy 7175 etching with the first bath, (c) Alloy 6061 etching with Bonderite® Smutgo NCB, (d) Alloy 6061 etching with the first bath, (e) Alloy 2024 etching with Bonderite® Smutgo NCB and (f) Alloy 2024 etching with the first bath.....	45
Figure 23. Sealing with hot water corrosion test repetition: (g) Alloy 7175, (h) Alloy 6061 and (i) Alloy 2024.....	46
Figure 24. Sealing with hot water dye spot test: (j) Alloy 2024 etching with Bonderite® Smutgo NCB, (k) Alloy 2024 etching with the first bath, (l) Alloy 7175 etching with Bonderite® Smutgo NCB, (m) Alloy 7175 etching with the first bath, (n) Alloy 6061 etching with Bonderite® Smutgo NCB and (o) Alloy 6061 etching with the first bath.....	48
Figure 25. Sealing with hot water dye spot test expansion.....	48
Figure 26. Potassium dichromate corrosion test with etching bath 1: (A) Alloy 2024, (B) Alloy 7175 and (C) Alloy 6061.....	50
Figure 27. Potassium dichromate corrosion test with etching bath 2: (D) Alloy 2024, (E) Alloy 7175 and (F) Alloy 6061.....	50

Figure 28. Bonderite® 1200S corrosion test with etching bath 1: (G) Alloy 2024, (H) Alloy 7175 and (I) Alloy 6061	51
Figure 29. Bonderite® 1200S corrosion test with etching bath 2: (J) Alloy 2024, (K) Alloy 7175 and (L) Alloy 6061	52
Figure 30. Fastening methods: (a) titanium rack and (b) wire.....	53
Figure 31. Bonderite® 1200S corrosion test repetition on the Alloy 2024	54
Figure 32. Potassium dichromate dye spot test: (Q) Alloy 2024 etching with Bonderite® Smutgo NCB, (R) Alloy 2024 etching with the first bath, (S) Alloy 7175 etching with Bonderite® Smutgo NCB, (T) Alloy 7175 etching with the first bath, (U) Alloy 6061 etching with Bonderite® Smutgo NCB and (V) Alloy 6061 etching with the first bath.....	56
Figure 33. Potassium dichromate dye spot test expansion	56
Figure 34. Alloy 2024 with primer after performing the dry paint adhesion test: (1) Bonderite® Smutgo NCB etching bath, (2,3) First etching bath.....	58
Figure 35. Alloy 7175 with primer after performing the dry paint adhesion test: (4) Bonderite® Smutgo NCB etching bath, (5,6) First etching bath.....	58
Figure 36. Alloy 6061 with primer after performing the dry paint adhesion test: (7) Bonderite® Smutgo NCB etching bath, (8,9) First etching bath.....	58
Figure 37. Alloy 2024 with primer plus top coat after performing the dry paint adhesion test: (10) Bonderite® Smutgo NCB etching bath, (11,12) First etching bath	59
Figure 38. Alloy 7175 with primer plus top coat after performing the dry paint adhesion test: (13) Bonderite® Smutgo NCB etching bath, (14,15) First etching bath	59
Figure 39. Alloy 6061 with primer plus top coat after performing the dry paint adhesion test: (16) Bonderite® Smutgo NCB etching bath, (17,18) First etching bath	59
Figure 40. Alloy 2024 with primer after performing the wet paint adhesion test: (19) Bonderite® Smutgo NCB etching bath, (20,21) First etching bath	60
Figure 41. Alloy 7175 with primer after performing the wet paint adhesion test: (22) Bonderite® Smutgo NCB etching bath, (23,24) First etching bath	60
Figure 42. Alloy 6061 with primer after performing the wet paint adhesion test: (25) Bonderite® Smutgo NCB etching bath, (26,27) First etching bath	61
Figure 43. Alloy 2024 with primer plus top coat after performing the wet paint adhesion test: (28) Bonderite® Smutgo NCB etching bath, (29,30) First etching bath	61
Figure 44. Alloy 7175 with primer plus top coat after performing the wet paint adhesion test: (31) Bonderite® Smutgo NCB etching bath, (32,33) First etching bath	61
Figure 45. Alloy 6061 with primer plus top coat after performing the wet paint adhesion test: (34) Bonderite® Smutgo NCB etching bath, (35,36) First etching bath	62

LIST OF TABLES

Table 1. Characteristics of the CAA, BSAA and TSA processes [6] [7] [8]	5
Table 2. Alloys' chemical composition [wt.%] [14].....	17
Table 3. Dimensions of the test specimens	18
Table 4. Bonderite® Smutgo NCB composition	22
Table 5. Comparison between the two etching baths	23
Table 6. Tank characteristics.....	25
Table 7. Components concentration	25
Table 8. Bonderite® 1200S composition	30
Table 9. Stripping solution.....	34
Table 10. TSA coating thickness	42
Table 11. CAA coating thickness of the alloy 7175	43
Table 12. CAA coating thickness of the alloy 2024	43
Table 13. TSA coating weight.....	44
Table 14. CAA coating weight.....	44
Table 15. Possible degrees of coloration.....	47
Table 16. Possible degrees of detachment.....	57

ABBREVIATIONS

AC	Activated Carbon
BSAA	Boric Sulphuric Acid Anodising
CAA	Chromic Acid Anodising
CCC	Chemical Conversion Coating
CMR	Carcinogenic, Mutagenic or Toxic for Reproduction substances
ECHA	European Chemicals Agency
ISO	International Organization for Standardization
OAC	Chromic Anodic Oxidation
PBT	Persistent, Bioaccumulative and Toxic substances
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SAA	Sulphuric Acid Anodising
SVHC	Substances of Very High Concern
TSA	Tartaric Sulphuric Anodising
UV	Ultraviolet
vPvB	very Persistent and very Bioaccumulative substances

1. Introduction

1.1. Scope of the project

The main objective of this thesis is to study an alternative anodising process without hexavalent chromium. The anodising process can be divided in three important successive steps. The first one is the surface conditioning before anodising which consist of a degreasing phase followed by an acid etching. Once the surface is ready the next step is to anodise and finally, when it is needed, different post-treatments can be applied.

Nowadays, unfortunately, hexavalent chromium compounds are widely used in the anodising process and they are present in the three stages. This thesis focuses on the analyses of chromium-free alternatives for the surface conditioning and for the anodising.

The alternative product studied, as a substitute of the current acid etching bath with sodium dichromate, is Bonderite® Smutgo NCB. It is analysed if the etching bath has influence on the final results and it is verified if the new product without chromium compromise or not the effectiveness of the anodising process.

The substitute bath analysed for the current Chromic Acid Anodising (CAA) is the Tartaric-Sulphuric Anodising (TSA) developed by Airbus. It is studied if the TSA is capable of producing an anodic coating film with the same resistance against corrosion and paint adhesion as the current CAA.

It is compared the thickness, the coating weight, the corrosion resistance and the loss of the absorption power achieved by the TSA anodic film with those obtained with the CAA, to see if the first process is a really good substitute for the second one.

It is also studied the compatibility of the TSA anodic film with various current post-treatments. It is tested three different sealings: with hot water, with potassium dichromate and with the chemical conversion coating Bonderite® M-CR 1200S Aero. On samples without sealing, it is checked the compatibility of an epoxy primer and a polyurethane topcoat in use by Airbus.

In order to verify if there is a significant difference between the performances obtained on different aluminium alloys, or otherwise, if the results obtained are similar regardless the composition and the thermal treatment of them, all the tests were performed on three different ones.

The three aluminium alloys chosen are widely used in aeronautic applications and they are representative of the 2xxx, 7xxx and 6xxx series, specifically, they are the AA2024-T3, AA7175-T7351 and AA6061-T6.

1.2. State of art

1.2.1. Chromium

Chromium is a lustrous, brittle and very hard transition metal whose symbol is Cr. It is a good conductor of electricity and heat, takes a high polish and has a good resistance against tarnishing and corrosion. Its melting and boiling points are high. Its elemental state is difficult to find in the environment but its compounds are present in the nature and it can also be mined as chromite, its most abundant mineral.

The health risks related to the exposure to chromium are dependent on its oxidation state. Chromium has a large number of them. The trivalent and the hexavalent forms are the most frequently found in its compounds, whereas +5, +4, +2 or lower oxidation states are more rare to observe.

The trivalent compounds are not considered a health hazard. Different studies have been conducted but they could not find enough evidences to prove that the trivalent chromium is carcinogenic [1]. Although in large amounts it can cause nose and mouth irritations and even skin rashes.

In contrast, the hexavalent chromium is a toxic and carcinogenic substance which can cause serious health problems. Exposure to it can produce respiratory problems, such as nosebleeds, nose irritation and lung cancer; in contact with the skin it can cause rashes, irritation, dermatitis and ulceration; if it is ingested produces upset stomachs, weakened immune systems, kidney and liver damage, alteration of genetic material; and even can cause death if the exposure is prolonged. [2]

Because of the health and the environment risks that the exposure to hexavalent chromium involves, progressively restrictions and rigorous controls have been imposed in the industries which use it in their processes.

1.2.2. REACH regulation

REACH is a European regulation for the Registration, Evaluation, Authorisation and Restriction of Chemicals. Its main objective is to provide protection against healthy and environmental risks that can be produced by some chemicals.

All the companies and industries have to prove to ECHA (European Chemicals Agency) that they are able to handle the risks related to the substances they use. When the hazards cannot be managed ECHA can restrict them in different ways and the most dangerous substances should be substituted with less harmful ones.

When a substance is considered to be hazardous it is incorporated into the list of Substances of Very High Concern (SVHC) [3]. They can be divided in three big groups depending on their harmful properties: Carcinogenic, Mutagenic or Toxic for Reproduction (CMR substances); Persistent, Bioaccumulative and Toxic (PBT substances); or very Persistent and very Bioaccumulative (vPvB substances). Once they are incorporated into this list the companies that use them must research and develop sustainable alternatives because they must be removed from the production in the near future.

Chromium hexavalent compounds were considered to be CMR substances and they were added in the SVHC list on 2010. In order not to affect the industry negatively and to ensure a progressively replaced of them, they were incorporated in the authorization list with a sunset date of 2017. These hexavalent compounds are: chromium trioxide and their acids and oligomers, such as chromic acid and dichromic acid; sodium dichromate; potassium dichromate; ammonium dichromate; potassium chromate and sodium chromate. [4]

Because of this regulation, there is the need to search and analyse new alternatives processes without chromium hexavalent compounds able to give the some performance of the current ones. It affects many industries, but especially the aeronautic sector, where the anticorrosive properties of these compounds are critical.

1.2.3. Chromates in the aircraft industry

Hexavalent chromium compounds, also known as Chromates, have been widely used in the aircraft industry during the last decades. Their most important applications in this sector are the protection of metallic surfaces thanks to their high corrosion resistance.

Chromates can be classified into three different groups depending on their applications: surface treatment processes, paint applications and electric and electronic uses. The most important are in the first and the second group.

The first group, surface treatments, involves processes such as: Chromic Acid Anodising (CAA); Chemical Conversion Coatings (CCC), like Bonderite® M-CR 1200S Aero; hard chrome plating; or acid etching products like sodium dichromate.

The second group includes all the processes related with paint applications, such as: external and internal paints, like different primers and topcoats; bonding primers; or sealants.

As it can be seen in Figure 1, the surface treatments and the paint process are the applications with the highest percentage of chromates. Only the CAA represents a 33% of total chromates used in the aeronautic sector, while the external paints and the basic primers represents a 31% each one. The

three of them together represent more than 90% of chromates in use nowadays in this sector, for this reason, there is a great motivation to seek and study alternative substitutes to these processes, especially for the CAA.

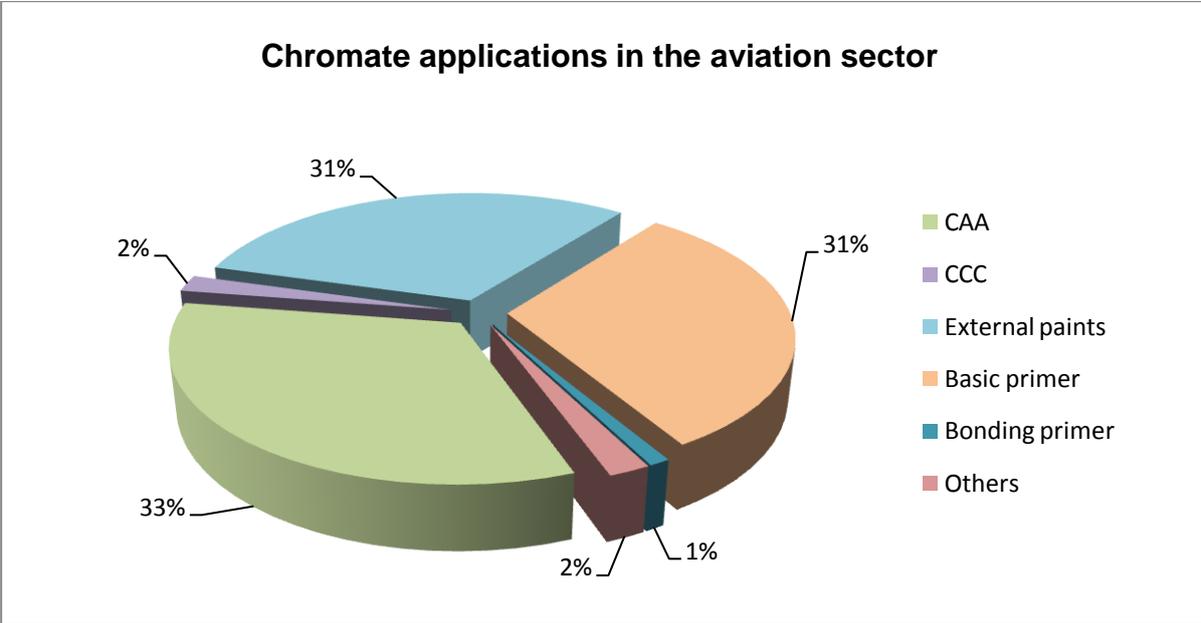


Figure 1. Chromate applications in the aviation sector [5]

1.2.4. Alternatives processes without chromates

Unfortunately, the substitution of the hexavalent chromium compounds for sustainable alternatives without compromising the technical quality and the performance in the aeronautic sector is a very hard work.

In the particular case of the anodising process, the alternatives must be able to give to the aluminium alloys the required corrosion protection, facilitate the adhesion of paint and be compatible with the post-treatments, and at the same time, they do not have to affect the fatigue life of the alloys.

Different alternatives have been studied, such as, Sulphuric Acid Anodising (SAA), Boric Sulphuric Acid Anodising (BSAA) or Tartaric Sulphuric Anodising (TSA). The second one was developed by Boeing and the third by Airbus, both of them seem to be the most promising alternative candidates. Table 1 presents their most basic characteristics. As it can be seen, the TSA and the BSAA present some advantages compared to the traditional chromic acid process. The time needed to achieve the required thickness is lower, it is reduced almost by half, and the voltage is also inferior.

Moreover, the treatments and the maintenance costs are reduced because their electrolytes are more sustainable and have a lower environment impact than the chromic acid electrolyte. Another important point that makes these alternatives attractive is that the current installations for the CAA are easy to adapt to the new ones doing minimal modifications.

Parameters	CAA	BSAA	TSA
Time	45 min	18 to 22 min	25 min
Temperature	38 to 42 °C	25 to 29 °C	36 to 39 °C
Voltage	21±1 V or 40±2 V	15±1 V	14± 1V
Thickness	3 to 5 µm	3 to 5 µm	3 to 5 µm
Electrolyte	65 g·l ⁻¹ chromic acid	45 g·l ⁻¹ sulphuric acid 8 g·l ⁻¹ boric acid	40 g·l ⁻¹ sulphuric acid 80 g·l ⁻¹ tartaric acid

Table 1. Characteristics of the CAA, BSAA and TSA processes [6] [7] [8]

In the case of paint applications, which also represent a large percentage of the chromates in use in the aviation sector, different sustainable alternatives are being studied too. In this field, the efforts are focus on the development of low Volatile Organic Compounds and water based formulations, in order to substitute the current solvent based primers and paints. [5]

2. Theoretical review

2.1. Aluminium and its alloys

2.1.1. Aluminium

Aluminium is the third most common element found in the earth's crust. Due to its reactivity, it is usually found combined with other elements such as iron, oxygen or silicon. The aluminium as metal is obtained from the bauxite ore using an economical procedure. It consists in obtaining alumina using the Bayer process with sodium hydroxide, followed by the alumina reduction to aluminium metal by means of electrolysis.

Although during the last years new high-performance composite materials have been developed, aluminium is still one of the most used materials in the aeronautics industry because it presents attractive characteristics for this sector. As an example, in the Figure 2, it can be seen the materials distribution of the Airbus A340 where the aluminium weight percentage represents more than 70%.

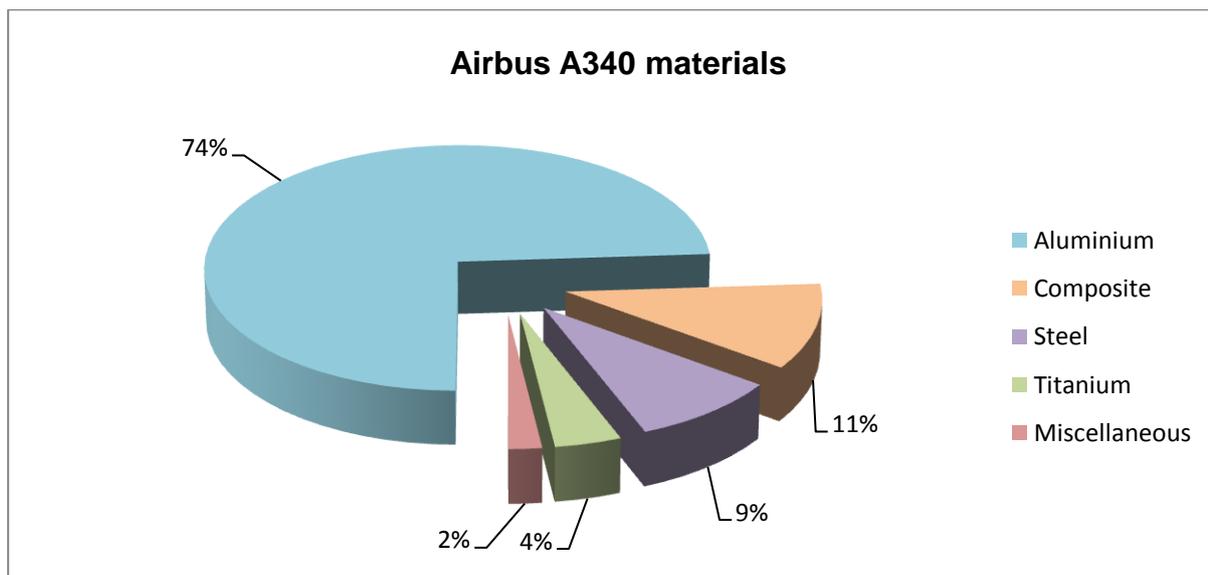


Figure 2. Airbus A340 materials [wt.%] [9]

Aluminium is interesting for the aircraft industry because it can achieved a high mechanical strength and is a very lightweight metal, whose density is $2.7 \text{ g}\cdot\text{cm}^{-3}$. The pure aluminium has high resistance against corrosion due to the oxide coating formed on its surface in contact with the oxygen. This layer is non-porous and water proof and it is able to protect the base material from future oxidations. Although this oxide layer has a good corrosion resistance against acid solutions it can be attacked by alkaline mediums. It can be improved by increasing its thickness using the anodising process. The mechanical strength of the pure aluminium is low, between 7 and 11 MPa, but it can achieve a high

one, around 690 MPa, by means of heat treatments and alloying. However, most of these alloying elements which increase its mechanical strength affect negatively its corrosion resistance. For this reason, it is necessary to apply surface treatments in order to achieve a good protection. [10]

2.1.2. Aluminium alloys

As it mentioned above, the pure aluminium has little interest for structural uses because it presents a low strength resistance. For this reason, in the industry is not used in its pure form but combined with alloying elements in order to improve its performance. The most common ones are silicon, magnesium, manganese, zinc and copper. Each one of them improves different specific properties. Silicon increases its mechanical strength and ductility and reduces the melting point. Magnesium as alloying reduces the melting point too and increments its corrosion resistance. Copper provides a high strength but it worsens its corrosion resistance, ductility and weldability. Manganese increases its strength with the advantage that does not affect its resistance against corrosion. And finally zinc gives a great mechanical strength and enables hot and cold precipitation hardening.

The aluminium alloys studied in this thesis are three: the AA2024-T3, the AA6061-T6 and the AA7175-T7351.

2.1.2.1. AA2024-T3

The AA2024-T3 is an aluminium alloy whose main alloying element is copper, as all the alloys of the 2xxx series. Its thermal treatment, T3, consists in a heat treatment followed by cold work and a naturally aged to a substantially stable condition. It has an ultimate tensile strength between 400 and 425 MPa, its yield strength is around 270 MPa and its elongation is in the range of 10 and 15%. It is one of the most used alloys in aircraft applications because of its high strength to weight ratio, its good resistance to fatigue crack growth along with high fracture toughness. However it presents a low weldability and an average machinability. It has a poor corrosion resistance, because of copper, and normally it is clad with aluminium or aluminium alloy with zinc in order to improve it, although, the fatigue resistance can be negatively affected. As said above, it is one of the most alloys used in the aircraft structure and in bottom parts of the wing.

2.1.2.2. AA6061-T6

The main alloying elements of the series 6xxx, such as AA6061-T6, are magnesium and silicon. The thermal treatment T6 gives to the alloy dimensional stability and consists in a heat treatment followed by an artificially age. It presents good mechanical properties and good resistance against corrosion. It can achieve a good finishing and has a high weldability. Its ultimate tensile strength and its tensile

yield strength are 310 MPa and 276 MPa, respectively, and can reach values of elongation between 12 and 17%. This aluminium alloy has various applications in the aircraft industry. It is used in areas where is required a resistant material, such as, the aircraft landing tape or the bottom parts of the aircraft where can be accumulation of fluids and liquids.

2.1.2.3. AA7175-T7351

The main alloying element of the alloy AA7175-T7351, as all the 7xxx alloys, is zinc. Its thermal treatment, T7351, increases its stress-corrosion resistance and consists in a heat treatment followed by a specially artificially aged. This aluminium alloy has a high tensile strength, between 430 and 480 MPa, its yield strength is in the range of 340 and 390 MPa and its elongation is around 7%. It presents great mechanical characteristics in terms of strength, toughness and fatigue. It has a good machinability although its hardenability is limited. Because of its characteristics and performance this alloy is widely used in aircraft structure in parts where high strength is required, such as upper surface of the wing or in the middle and upper parts of the fuselage.

2.2. Anodising process

Aluminium in contact with the oxygen produces a natural thin oxide layer called alumina, Al_2O_3 , whose thickness is in the order of 0.02 μm . It provides relatively good natural protection against atmospheric conditions and tends to be regenerated when the metal is eroded avoiding subsequent corrosion.

But the natural layer is not always able to protect the metal and prevent the appearance of corrosion points. The corrosion behaviour of the aluminium alloys is sensitive to the small amount of impurities in the metal. The natural oxide layer has a heterogeneous and irregular nature that affects its protective properties. This can be solved by increasing the thickness of the alumina layer artificially through the anodising process. This treatment is able to generate a layer that provides excellent protection against corrosion and also increases the adhesion of organic coatings compared with the bare metal.

The anodising is an electrochemical process that consists in obtaining a protective layer of alumina on the aluminium by means of passing current flow through an acid or alkaline electrolytic solution. The anodic film grows from the substrate thanks to the electrochemical process, so it is integrated into the metal and has a great adhesion. It grows 50% up to the surface and 50% depth so it has to be into account the dimensional increase. The anodising process can be divided in three important successive steps. The first one is the surface conditioning before anodising which consist of a degreasing phase followed by an etching. Once the surface is ready the second step is to anodise and finally the third and last step is the application of the post-treatments.

2.2.1. Pre-treatments

The surface preparation is really important and cannot be underestimated, without a good conditioning the performance and the quality of the rest of the subsequent processes could be affected and the required results could not be achieved.

2.2.1.1. Degreasing and cleaning

Degreasing and cleaning are the first processes before performing the rest of the surface treatments. The main objective of them is to remove any traces of dirt that can be deposited on the metal surface during the manipulation or transportation of the material. The main dirties found on the aluminium surface are: marking inks, grease, lube oils, polishing residues, finger marks, metal chips, welding or brazing fluids. This cleaning is necessary in order to achieve a good anodic reaction and to get a uniform aluminium oxide layer.

The most current methods used are the alkaline degreasing products. They are the substitutes of the vapour degreasing methods based on chlorinated and fluorinated solvents which are obsolete due to ecological concerns. However, a part of the alkaline degreasing products, there are ultrasonic cleaning methods, although they are normally used in particular cases when the other ones are not suitable.

Nowadays, there are a lot of alkaline degreasing products in the market. Their main compounds are usually sodium hydroxide, corrosion inhibitors and wetting agents. They have to be appropriated to the metals and their attack to them must be minimized and controlled. In the case of aluminium their pH should remain between 9 and 11. They should have high rinsing performance, high solubility, good wetting properties and a great emulsifying power.

Ultrasonic cleaning methods require expensive equipment and they are more suitable when the parts to be cleaned are small. They are used when the cleaning is difficult and the immersion methods are not good enough. [11]

2.2.1.2. Etching

The controlled etching of the surface is a critical step in the process. It consists in removing the aluminium oxides that may be present on the surface in different quantities and forms and replaced them by a thin and uniform coating in order to provide a uniform base for the anodising. There are two different types of etchings: the alkaline etching and the acid etching. Their rate of etching depends on the concentration of the product and on the operating temperature.

The alkaline etching bath is normally composed by an aqueous solution of sodium hydroxide, with a concentration of 5 to 10% and an operating temperature between 40 and 50 °C. It is the most economical etching method. The drawback is that it requires another subsequent process with nitric acid, especially in the case of aluminium alloys with copper, in order to remove the insoluble products generating during the alkaline etching. For this reason, it is rarely used in the aviation sector.

The acid etching has been traditionally performed using a solution composed of sulphuric acid, hydrofluoric acid and sodium dichromate at room temperature. This last component, like all hexavalent chromium compounds, is considered hazardous and carcinogen. Because of the health concerns about them, alternative products have been developed based on phosphoric and sulphuric acid solutions. In the aeronautic sector the most new favourable formulations are composed by sulphuric acid, ferric sulphate and acid nitric, for example, the Bonderite® Smutgo NCB studied in this thesis.

2.2.2. Anodising

As explained above, the anodising consists in the oxidation of the aluminium surface: the aluminium metal is converted to aluminium oxide or alumina. Figure 14 shows the schematic of the device needed to perform the anodising. It consists of two electrodes connected to a current rectifier and immersed in an electrochemical cell containing an electrolyte. In order to control the intensity and the voltage of the process, an ammeter is connected in series and a voltmeter in parallel. The aluminium acts as an anode and it is where the oxidation occurs. The cathode, whose function is to close the electrolyte circuit, is usually of steel or lead, although this last one has fallen into disuse. When the electric current is applied to the system the electrons flow from the anode to the cathode leaving cations on the aluminium alloy surface.

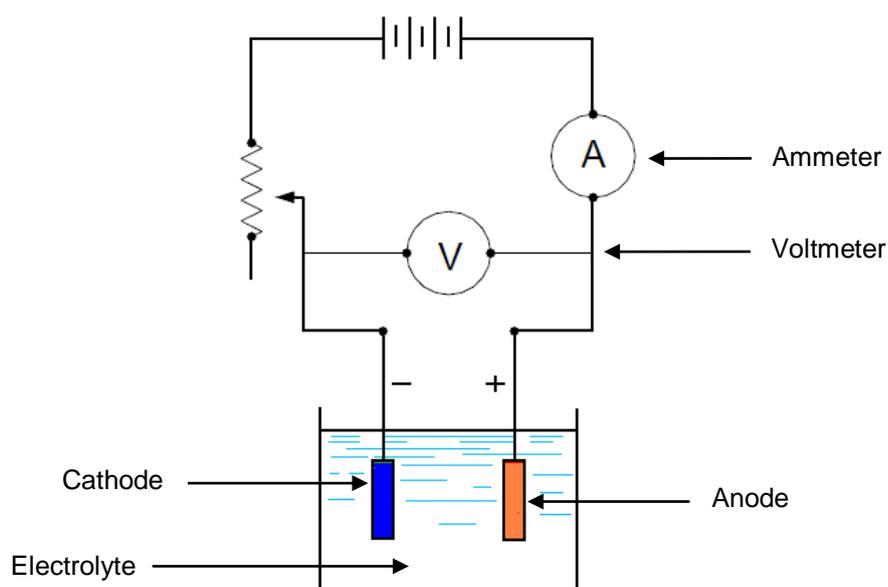
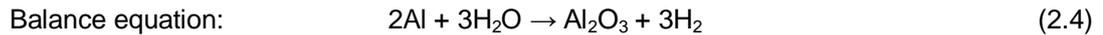
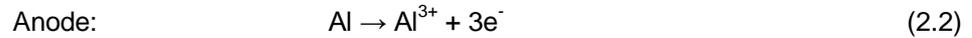
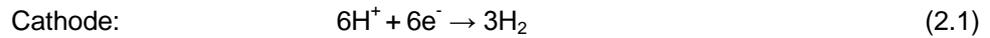


Figure 3. Electrochemical cell

If the electrolyte is an acid solution, the oxygen from the electrolytic dissociation of the water will react with the cations of the anode in order to produce alumina on the surface of the alloy. The reactions that take place are the followings:



The conversion process of the aluminium is determined by the time and the electric current density of the anodising, if these parameters increase the conversion increases too. The morphology and the thickness of the anodic film also depend on the voltage, temperature and electrolyte composition.

2.2.2.1. Anodic film structure

There are different factor that will affect the anodic film structure. The most important ones are the electrolyte composition and the anodising conditions, such as: the temperature, the voltage or the duration of the process. However, the anodic film structures can be classified in two main groups: the barrier films and the porous films, see Figure 4.

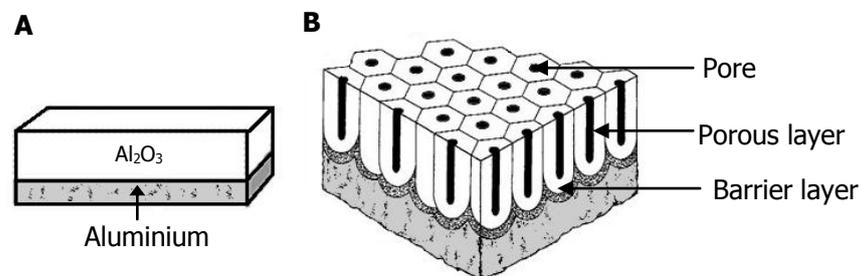


Figure 4. Anodic film structure: (A) Barrier anodic film, (B) Porous anodic film [10]

2.2.2.1.1. Barrier anodic films

The barrier anodic films are generated in electrolytes whose pH is near neutral, between 5 and 7, where the aluminium is passive, such as solutions of boric acid with sodium borate or ammonium tartrate. These electrolytes do not have solvent action on the aluminium oxide layer, for this reason a thin oxide film is formed on the surface. These films grow uniformly along the surface of the aluminium alloys. They are really adherent and non-conductive. The oxide growth takes place until its electrical resistance is so high that the current flow cannot circulate to the anode, its thickness depends mainly on the voltage applied. Due to its dielectric properties are widely used in the electronics industry.

2.2.2.1.2. Porous anodic films

The porous anodic films are generated in electrolytes whose pH is in the range where the aluminium oxidation occurs, such as sulphuric acid, chromic acid or tartaric-sulphuric solutions. Thanks to electron microscopy studies it has been observed that the anodic film is composed of two different layers: a thin, dense and compact internal layer called barrier film and another one external and porous.

The barrier film is generated during the first minutes of anodising. Its thickness is approximately between 0.1 and 2% of the total anodic film and it depends directly on the voltage applied and inversely on the rate of dissolution of the oxide in the electrolyte. This film is not porous and because of its microstructures failures is conductive. When the barrier film reaches its limit thickness, over its surface a continuous porous film is generated. Because of the porous nature, this layer increases its thickness during the anodising whereas the barrier film thickness remains constant. The aluminium oxidation and dissolution occurs through the pores, and as can be deduced from the film existence, the oxidation rate is higher than the dissolution. In Figure 5 it can be seen the porous film using a scanning electron micrograph.

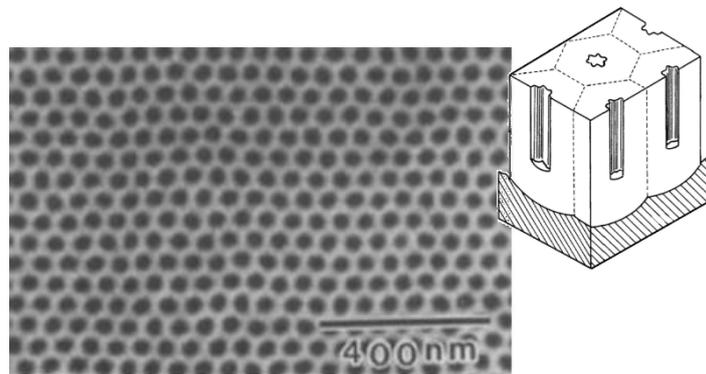


Figure 5. Scanning electron micrograph of the porous anodic film [10]

2.2.2.2. Electrolytes

The electrolytes usually are acid solutions, although it is possible to anodise in alkaline media. The most acid electrolytes used are the sulphuric acid, the chromic acid, the oxalic acid and the phosphoric acid. In the industry the most widely used is the sulphuric acid, but in the aeronautic sector is the chromic acid. As an alternative to this last electrolyte, Airbus has developed the tartaric sulphuric anodising and Boeing the boric sulphuric anodising. In the next section it is detailed the main characteristics of the two electrolytes studied in this thesis: the chromic acid and the tartaric sulphuric.

2.2.2.2.1. Chromic acid electrolyte

Chromic acid anodising was the first anodising process developed. It was invented by Bengough and Stuart in 1923. It is the most used in the aircraft industry because presents different characteristics that make it suitable for this sector. The most important one is that the chromic acid is the electrolyte that less affects the fatigue strength of the aluminium alloys, being convenient in cases where the fatigue strength is critical. Also it is less aggressive to the aluminium than other electrolytes and its rinsing and removal after the anodising is easier.

The common operating parameters for this kind of anodising in the aircraft sector are the followings. The temperature of the electrolyte is between 38 and 42°C and the concentration of chromic acid is in the range of 30 to 60 g·l⁻¹. The cathode normally is made of mild steel or stainless steel. The anodising current density achieved approximately is between 0.3 and 0.4 A·dm⁻². In Figure 6 it can be seen the three most typical electrolytic cycles for this process. The use of them depends mainly on the aluminium alloy. The electrolytic cycle A is normally used on aluminium alloys of the 6xxx series and the electrolytic cycle B on alloys of the 2xxx and 7xxx series. The last one, the electrolytic cycle C called Bengough is an alternative process to the other two. [6]

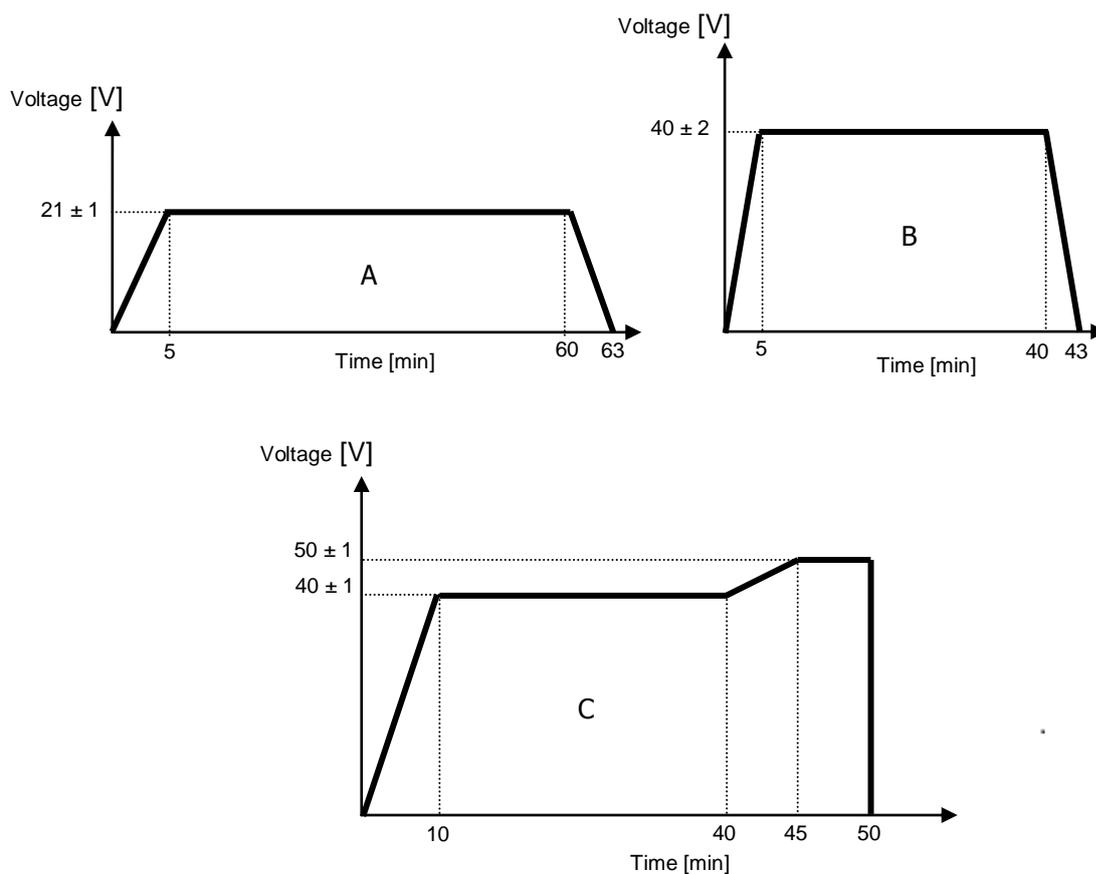


Figure 6. CAA electrolytic cycle [6]

2.2.2.2. Tartaric sulphuric electrolyte

The tartaric sulphuric anodising has been developed by Airbus in order to obtain an anodising process without hexavalent chromium able to achieve the same performance of the chromic acid anodising.

Apart of being a chromate-free process it presents some other technical advantages respect to the traditional one. The time needed to achieve the required thickness is lower, it is reduced almost by half, and the voltage is also inferior. Moreover, the treatments and the maintenance costs are reduced because their electrolytes are more sustainable and have a lower environment impact than the chromic acid electrolyte. Another important point that makes this alternative attractive is that the current installations for the CAA are easy to adapt to the new ones doing minimal modifications.

On the other hand, the main disadvantage of the tartaric sulphuric anodising is the fungus growth in the treatment line because the electrolyte is less harmful. In order to avoid fungal contamination the installation requires activated carbon filters (AC filter). If the filters are not enough and the appearance of fungus is persistent should be taken additional measures, for example, installation of ultraviolet lamps (UV lamps).

During the anodising the temperature of the tartaric sulphuric electrolyte must be between 36 and 39°C and the nominal concentrations of sulphuric and tartaric acid are 40 g·l⁻¹ and 80 g·l⁻¹, respectively. The current density during the process is in the range of 0.6 and 1 A·dm⁻². In Figure 7 it can be seen its electrolytic cycle.

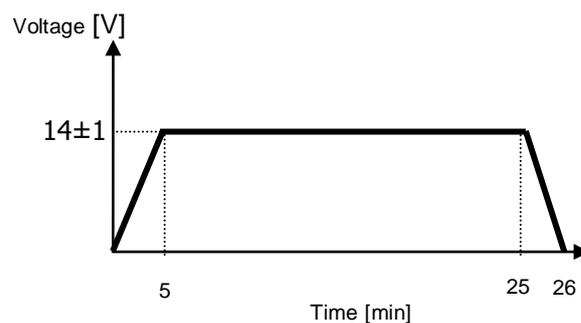


Figure 7. TSA electrolytic cycle [12]

2.2.3. Post-treatments

2.2.3.1. Sealing with hot demineralised water

As mentioned above the anodic film obtained after the aluminium anodising is porous and has absorbent properties, for this reason is not protective enough against corrosion. In order to improve the properties of the anodic film, one possible post-treatment is sealing with demineralised water. It consists in immersing the aluminum in hot demineralised water in order to hydrate the alumina and close the porous structure. The aluminium oxide is converted into a stable layer called boehmite, AlOOH. The reaction that takes place is the following:



The conversion of aluminium oxide to boehmite involves an increase in volume able to close to porous, accompanied by a significant decrease in electric capacity and a large increase of its electrical resistance.

The sealing rate depends on the temperature of the demineralised water. The higher and most efficient rate is achieved between 98 and 100°C. Apart from the temperature, the sealing also depends on the water pH which should be between 5 and 7 where the alumina is stable. The time needed to obtain a good quality sealing varies according to the film thickness, the pore diameter and the specific properties of the aluminium oxide. A time between 20 and 60 minutes is enough, for example, in the case of the tartaric sulphuric anodising Airbus recommends a time of 40 minutes.

2.2.3.2. Chemical Conversion Coatings (CCC)

The chemical conversion coatings are protective and adherent layers whose main objective is to improve the adhesion between the organic coating and the aluminium alloys surface. They also provide protection against corrosion and are used as a treatment in areas where the anodic film is damage or in parts where is difficult to get a good anodising of the surface because of their shape.

The chemical conversion coatings are based on oxidation-reduction reactions of different reagents with the aluminium alloy surface. They can be divided in two main groups: phosphate conversion coatings and chromate conversion coatings. In the aircraft industry is used the last group, mainly the Bonderite® 1200S. Due to the health risks related with chromates new alternative products are being studied, such as Bonderite® 5700, Nabutan STI/310 or Iridite NCP. [13]

2.2.3.3. Organic coatings

The organic coatings in aeronautical applications are composed by two layers, a primer and a topcoat. Their main function is to protect the aluminium alloy of oxygen, ions and water. In case that some agent was able to penetrate into the coating they must act as corrosion inhibitors too. Between the metal and the organic coating is applied a conversion coating whose main functions are to improve the adhesion between them and provide some corrosion resistance. The conversion coating can be an anodic film or a chemical conversion coating.

The primers are applied directly on the conversion coating and their main function is to give resistance against corrosion. Nowadays, they are chromate products and can have around a 25% of chromate inhibitors. The most used is strontium dichromate. The topcoats protect of mechanical damage and some of their components are UV absorbers in order to avoid coating photodegradation.

3. Experimental procedure

All the treatments and tests presented in this thesis were carried out in the Special Process Engineering installations of *OGMA-Indústria Aeronáutica de Portugal* in Alverca. The pilot plan, shown in Figure 8, consists of five lines of tanks designed to hold different surface treatments of aluminium, titanium and ferrous alloys.



Figure 8. OGMA's facilities

3.1. Test specimen definition

3.1.1. Materials

One of the objectives of this work is to study the compatibility of the TSA anodising on different aluminium alloys. For this reason, the chosen ones are the most representative of each aluminium series and the most widely used in the aviation sector. The tests were carried out using aluminium alloys from the series 2xxx, 6xxx and 7xxx, specifically AA2024-T3, AA6061-T6 and AA7175-T7351. Their chemical composition and their thermal treatment are detailed below.

As it can be seen in Table 2, the most important alloying element of the AA2024-T3 is copper, of the alloy AA6061-T6 are magnesium and silicon and of the alloy AA7175-T7351 is zinc.

Aluminium alloy	wt. %	Al	Cr	Cu	Fe	Mg	Mn	Si	Ti	Zn
AA2024-T3	Min	90.7	0	3.8	0	1.2	0.3	0	0	0
	Max	94.7	0.1	4.9	0.5	1.8	0.9	0.5	0.15	0.25
AA6061-T6	Min	95.8	0.04	0.15	0	0.8	0	0.4	0	0
	Max	98.6	0.35	0.4	0.7	1.2	0.15	0.8	0.15	0.25
AA7175-T7351	Min	87.1	0.18	1.2	0	2.1	0	0	0	5.1
	Max	91.4	0.28	2	0.5	2.9	0.3	0.4	0.2	6.1

Table 2. Alloys' chemical composition [wt.%] [14]

The thermal treatments of the studied alloys are T3, T6 and T7351. The first one, T3, is a thermal treatment applied to improve the strength of materials which have been cold work. It consists in a heat treatment, followed by the application of cold work and finally the aluminium is naturally aged until a stable condition. The second one, T6, consists in a heat treatment followed by an artificially aged. It increases the dimensional stability. And the last one, the thermal treatment T7351, improves the resistance of the aluminium to stress-corrosion and consists in heat treatment followed by a specially artificially aged.

In the next sections in order to simplify, the different aluminium alloys will be called without the thermal treatment, for example, the AA7175-T7351 will appear as AA7175.

3.1.2. Dimensions

For the performance of the tests it was used the samples available in OGMA's laboratory whose dimensions are shown in Table 3. In the case of the AA2024, there were two available dimensions. The biggest one was used for paint and sealing with hot water tests and the smallest one for the rest of them.

Aluminium alloy	Dimensions [mm]	Area [$\text{mm}^2 \cdot \text{surface}^{-1}$]
AA2024	125x80x1 to 4	10000
	250x75x0.5	18750
AA6061	250x75x0.8 to 1.3	18750
AA7175	125x80x1 to 4	10000

Table 3. Dimensions of the test specimens

3.2. Test specimen preparation process

The samples preparation process before performing the quality tests can be divided in three important steps: the pre-treatments, the anodising itself and the post-treatments.

As it can be seen in Figure 9, the pre-treatments consist of an alkaline pre-degreasing, followed by an alkaline degreasing and an acid etching. After each bath it is really important to rinse well the samples and remove all the products, otherwise, if some products remain on the specimen they could damage the surface and contaminate the next bath. For the last pre-treatment, acid etching, two different bath were studied: the first one is the most widely used and has a hexavalent chromium compound, sodium dichromate, and the second one was studied as an alternative to the first one with a non-chromate product, the Bonderite® Smutgo NCB.

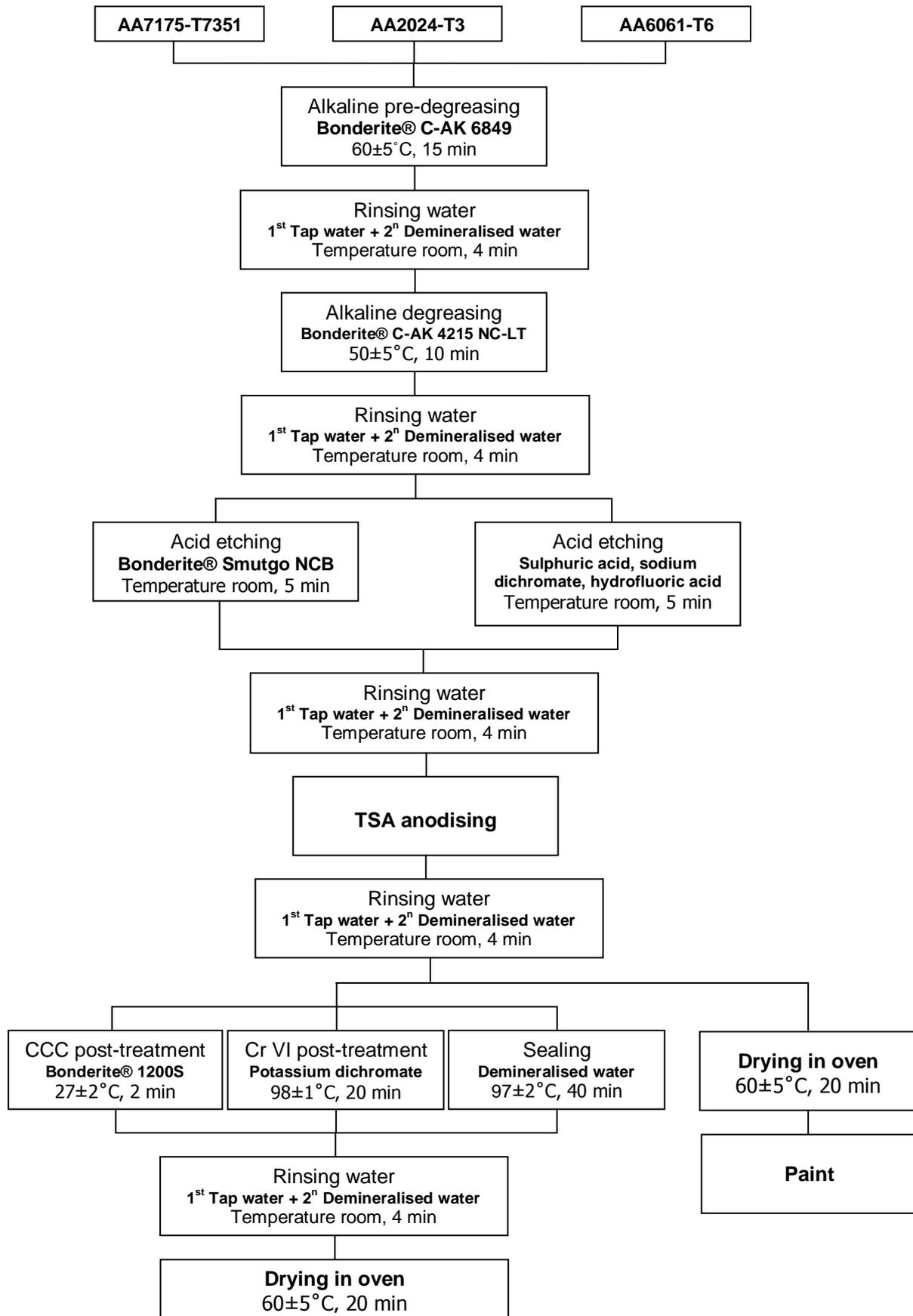


Figure 9. TSA anodising process

Once the pre-treatments have been applied and the samples have been rinsed, they are ready to be anodised. After the anodising and the proper rinsing, the post-treatments can be applied. It was studied the compatibility of three different current sealings: with demineralised hot water, with Bonderite® 1200S and with potassium dichromate. After their application the samples finally are rinsed and dried in oven.

The process followed in the case of the painted samples is slightly different. After the anodising and the proper rinsing the specimens are immediately dried. And they are painted within 24 hours after the anodising treatment.

3.2.1. Test specimen pre-treatments

The surface preparation before anodising is really important in the process because it directly affects the anodic film quality and the effectiveness of the post-treatments. In this case it consists of three successive steps: an alkaline pre-degreasing, an alkaline degreasing and an acid etching.

In the following sections there is a description of each step, explaining their applications and the products used.

3.2.1.1. Alkaline pre-degreasing

The first step is to immerse the test specimen an alkaline pre-degreasing bath. Its main goal is remove marking inks, grease and lube oils from the surface.

The product that was used is the aqueous alkaline degreaser Bonderite® C-AK 6849 AERO manufactured by Henkel which is a free chromate product. For the preparation of the immersion bath it is necessary to add Bonderite® 6849 at 10 to 20% by volume to water. Its operating temperature is from 55° to 70°C, for this reason the tank has a temperature control system that keeps it at 60±5°C. The bath is also equipped with an air agitation system and an oil and grease removal system for prolonging its service life.

The immersion time depends on the amount of contaminants on the aluminium alloy surface. It usually is between 15 and 30 minutes. The surface of the test specimens is relatively clean, for this reason they were immersed 15 minutes.

After the immersion in the pre-degreasing bath the test specimens have to be rinsed at least for 3 minutes. In this particular case, they were immersed in two subsequent baths. The first one with tap water for 2 minutes and the second one with demineralised water for 2 more minutes to ensure that the entire product was removed.

The next step after rinsing the specimens is to immerse them in the alkaline degreasing bath. It is important to keep the samples always wet along the process and do not let them dry to prevent contamination.

3.2.1.2. Alkaline degreasing

After the pre-degreasing, the test specimens were immersed in the alkaline degreasing bath. The product used was Bonderite® C-AK 4215 NC-LT manufactured by Henkel. It is an aqueous free chromate solution which attacks the aluminium slightly. The main function of this alkaline cleaner is to remove all grease and oils that may be left after the first bath.

The product concentration in the bath should be between 45 and 60 g·l⁻¹. Its operating temperature is from 45 to 55°C, for this reason the tank has a temperature control system that guarantees this range. It is also equipped with an air stirring system and an oil and grease removal. The immersion time in the bath should be between 5 and 10 minutes. In this case, an immersion of 10 minutes was enough to provide a good superficial cleaning.

As in the previous step, after the degreasing bath the samples were rinsed first in tap water and then with demineralised water following the same procedure.

3.2.1.3. Acid etching

Apart from removing the oils and grease, it is necessary to remove the oxides present on the surface to provide a uniform base for the next step, the anodising. This is needed because in addition to contaminants, aluminium oxides may be present on the surface in different quantities and forms. These oxides have to be removed and replaced by a thin and uniform oxide coating. This is reached by a controlled acid etching of the surface.

The most widely bath for this process is a solution composed of sulphuric acid, hydrofluoric acid and sodium dichromate. This last component, like all hexavalent chromium compounds, is considered hazardous and carcinogen. As the main objective of this thesis is the development a chromate VI-free process, it was studied an alternative product: the Bonderite® Smutgo NCB.

All the tests were performed with the two products to verify that the use of the new one does not compromise the effectiveness of the anodising and to confirm that the same results are achieved with both of them, in order to demonstrate that the Bonderite® Smutgo NCB is a good non-chromate substitute.

The nominal concentration in the first bath is $79 \text{ g}\cdot\text{l}^{-1}$ of sulphuric acid, $42 \text{ g}\cdot\text{l}^{-1}$ of sodium dichromate and $1.13 \text{ g}\cdot\text{l}^{-1}$ of hydrofluoric acid. It is also necessary to control the amount of Cu and Al to ensure that their levels in the bath are below $0.20 \text{ g}\cdot\text{l}^{-1}$ and $17.22 \text{ g}\cdot\text{l}^{-1}$, respectively. It works at room temperature, so it does not need any temperature control system. However, it requires a stirring system. The immersion time of the samples in this bath was 5 minutes.

The Bonderite® Smutgo NCB is a dark brown liquid and is formulated to deoxidize and desmut aluminium alloys, like the first bath. Its operating temperature is between 10 and 50°C . It requires a stirring system. According to the manufacture, the concentration in the bath should be between 22 to 28% of product in water. Its nominal etch rates are in the range of 2.54 to $22.86 \mu\text{m}/\text{surface}/\text{hr}$. The immersion time, as in the first bath, was 5 minutes. In Table 4 it can be seen its composition.

Component	Percentage [%]
Ferric sulphate	30-60
Nitric acid	5-10
Sodium hydrogendiflouride	1-5
Sulphuric acid	0.1-1

Table 4. Bonderite® Smutgo NCB composition

All the previous baths are part of the production line, so it was not necessary to manufacture them. But the Bonderite® Smutgo NCB is a new product. For this reason, in order to perform the tests a small bath, large enough for the immersion of the tests specimens, was manufactured. As shown in Figure 10.



Figure 10. Bonderite® Smutgo NCB bath

In Table 5, there is a comparison of the most important characteristics of each bath. Their etching rates on the AA2024 were provided by OGMA's chemical laboratory. As it can be seen, the difference between them lies on their composition because the rest of parameters are similar. Both of them need a stirring system, work at room temperature and an immersion time of 5 minutes is enough to achieve a good etching.

		Etching Bath 1	Etching Bath 2
Products		79 g·l ⁻¹ sulphuric acid 42 g·l ⁻¹ sodium dichromate 1.13 g·l ⁻¹ hydrofluoric acid	250 ml·l ⁻¹ Bonderite® Smutgo NCB
Chromium Compound		Yes	No
Stirring system		Yes	Yes
Temperature control system		No (Room temperature)	No (Room temperature)
Immersion Time		5 min	5 min
Etching rate on the AA2024	Sample 1	1.501 µm/surface/hr	1.561 µm/surface/hr
	Sample 2	1.502 µm/surface/hr	1.772 µm/surface/hr
	Sample 3	1.351 µm/surface/hr	1.739 µm/surface/hr

Table 5. Comparison between the two etching baths

After the etching bath the tests specimens were rinsed with tap and demineralised water for about 4 minutes, in order to remove all the products before the anodising.

In the next sections in order to simplify, the acid etching bath of sulphuric acid, hydrofluoric acid and sodium dichromate will be named Bath 1 and the Bonderite® Smutgo NCB bath will be called Bath 2.

3.2.2. Test specimen anodising

Once all the pre-treatments are completed the next step is the anodising of the samples.

3.2.2.1. TSA anodising installation

In order to perform the anodising tests, it was added in one of the lines of the plant a small provisional tank equipped with all the necessary items for the anodising, as it can be seen in Figure 11. The TSA anodising installation consists of the following equipment:

- Tank: it must be chemical resistant to acids. The suitable materials are PVC, PVDF, polyethylene or polypropylene. In this case the tank was made of polypropylene and its dimensions were 430 x 250 x 590 mm.
- Cathode: it was made of stainless steel AISI 316L. It also could be made of stainless steel AISI 321 or lead. The maximum ratio cathode/anode must be between 1:5 and 10:1.

- Stirring: there are two different possible stirring mechanisms for this kind of bath, air stirring and mechanical stirring, both of them are suitable if they are capable to homogenise properly the solution. Because of the dimensions of the tank it was chosen the air stirring. The agitation was done insufflating filtered air through a perforated tube placed in the bottom of the tank. The air flow was kept at minimum to prevent fungal growth.
- Rectifier: the generator must be capable to provide $1A \cdot dm^{-2}$ for parts to be anodised from 0 to 14 volts with an accuracy of $\pm 1V$.
- Heating system: the tank was equipped with a temperature control system composed by a resistance and a temperature sensor in order to guarantee a range of temperatures between 36 and 39°C.
- Anodic bar: it is where the samples to be anodised are linked. It is essential to have a good contact between the anodic bar and the frame of the test specimens. Because of the dimensions of the tank it was used wire as frame, it provides sufficient electrical conductance for the anodising process.
- Control of electrolytic cycle: the bath should have an ammeter and a voltmeter with an accuracy of $\pm 5\%$.

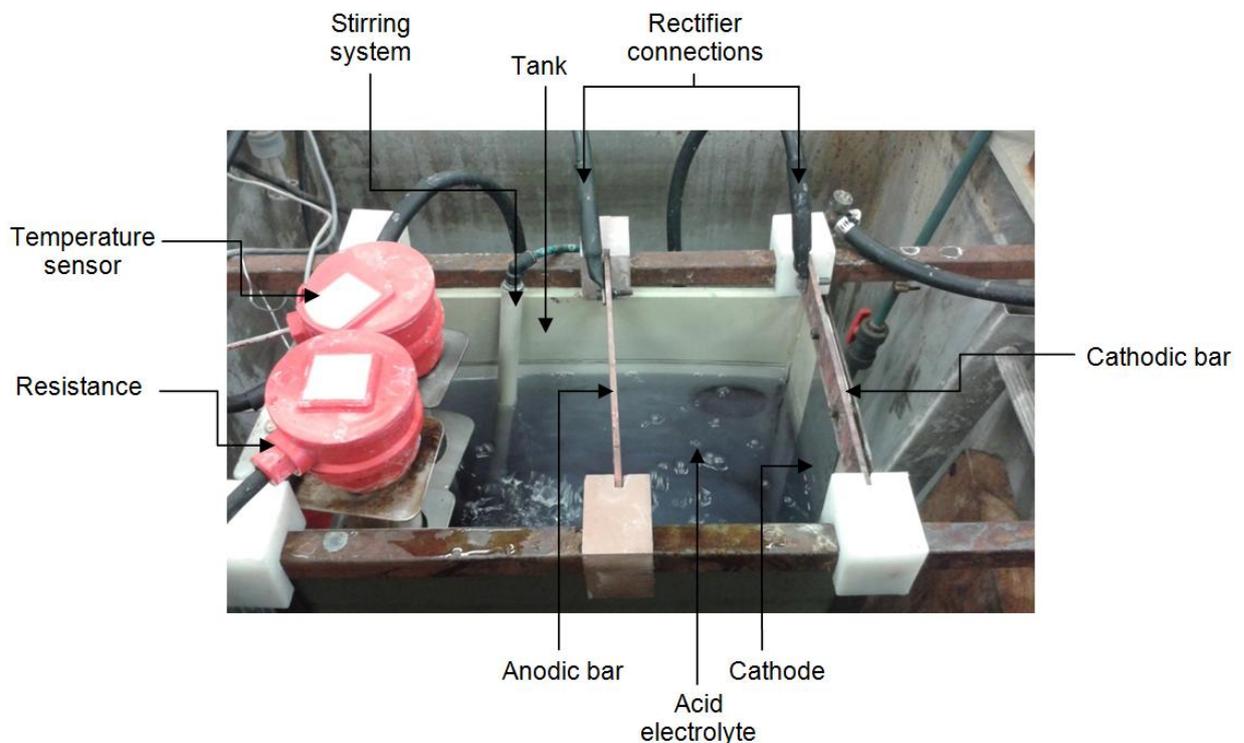


Figure 11. TSA anodising bath

The anodising tank used for the tests was the small dimensions, but in the production line because of the dimensions of the parts to be anodised it must be bigger. For this reason, it is necessary that the tank has an extractor system to remove the vapour emitted during the anodising process.

In this kind of bath could be fungus growth because the electrolyte is less noxious and it facilitates their proliferation. In consequence, baths with a long service life have to be equipped with an antifungal system. It can be consisted of filtering elements of active carbon or ultraviolet lamps. As it can be seen in Figure 11, the bath used had not any of these systems due to it was just a provisional one and its service life was short.

3.2.2.2. Bath manufacture

First of all, for the manufacture of the bath, it is necessary to calculate the bath volume which is determined by the work level and the dimensions of the tank, see Table 6. The work level must be high enough to immerse completely the resistance, otherwise it could be damage.

Characteristics	Dimensions
Tank dimensions	430 x 250 x 590 mm
Tank area	1075 cm ²
Work level	500 mm
Bath volume	54 l

Table 6. Tank characteristics

After determining the bath volume, it is calculated the amount of sulphuric and tartaric acid required for the volume of water from the tank, taking into account the nominal concentration values presented in Table 7.

Components	Concentration	
	Nominal [g/l]	Work [g/l]
Sulphuric acid	40	36-44
Tartaric acid	80	72-88

Table 7. Components concentration

The amount of tartaric acid required is 4.3 kg, it can be calculated from the Equation 3.1. For determining the amount of sulphuric acid it is necessary to know its density, 1.84 g·cm⁻³, the result is 1168.48 ml as shown in Equation 3.3.

$$C_4H_6O_6 = 80 \frac{g}{l} \cdot 53.75l = 4300g = 4.3 \text{ kg} \quad (3.1)$$

$$H_2SO_4 = 40 \frac{g}{l} \cdot 53.75l = 2150g \quad (3.2)$$

$$H_2SO_4 = 2150g \cdot \frac{1cm^3}{1.84g} = 1168.48 \text{ cm}^3 = 1168.48 \text{ ml} \quad (3.3)$$

Once calculated the amount of products, the bath is prepared as follows. First of all, it is important to ensure a proper cleaning of the tank and its equipments. The next step is filling the tank about an 80% of its volume with demineralised water and connecting the agitation system. Then, the amount of tartaric acid required is weighed and the amount of sulphuric acid is measured using a graduated cylinder. Finally, they are added in the bath taking into account the large release of heat caused by the sulphuric acid and the bath level is completed with demineralised water.

3.2.2.3. Bath analysis

After preparing the bath is always necessary to perform an analysis to verify that the concentrations of tartaric and sulphuric acid are correct and see if it necessary to add more quantity of any of them in order to meet the required concentrations.

Both components of the anodising electrolyte can be determined by two successive titrations. A titration consists in determining the unknown concentration of one solution by adding slowly another one of a known concentration until the reaction reaches the end point.

The recommended way to perform these two titrations by Airbus is using an automatic titroprocessor in order to achieve the required precision in the concentration determinations. At the time of the analyses, the laboratory did not have any available one, for this reason, the bath analyse was carried out manually with a titroprocessor.

The objective of the first titration is to determine the amount of total acid. It consists in pipet 1 ml of sample into a 250 ml beaker and add about 100 ml of distilled water and 2 ml of KF solution with a 300 g/l concentration. Then it is titrated with 1N NaOH solution on a titroprocessor with a combined glass-electrode, filled with 3N KCl solution in water as sensor. The strongest step in the titration curve indicates the titration end point in which all hydrogen ions are dissociated from the acid molecules.

As it can be seen in Figure 12, the titration was repeated 5 times in order to calculate the average consumption of solution. The first titration was dismissed because it only was used to know where approximately the strongest step occurs in order to obtain accurate results in the next titrations.

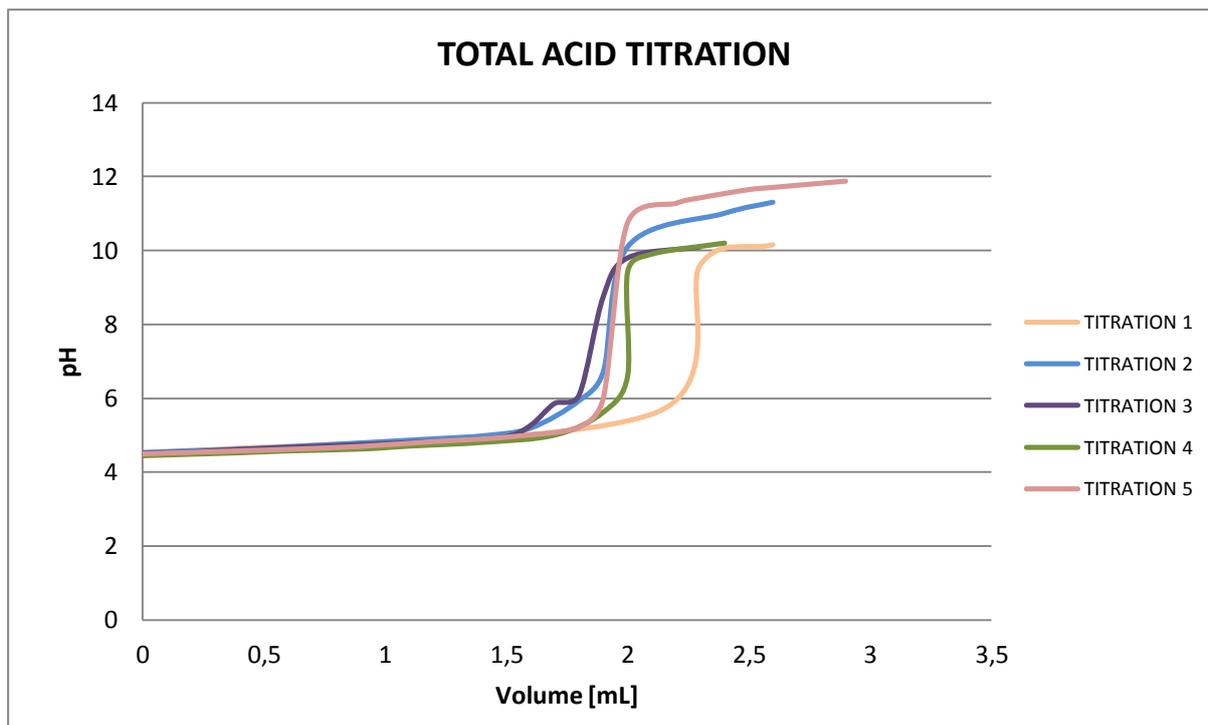


Figure 12. Total acid titration

Calculating the average consumption of NaOH solution, the amount of total acid can be calculated as shows Equation 3.4.

$$\text{Total acid [g/l]} = \text{titrated average volume [ml]} \cdot 49 = 1.95 \text{ ml} \cdot 49 = 95.55 \text{ g/l} \quad (3.4)$$

The second titration calculates the amount of sulphuric acid. The procedure is very similar to the previous one. In this case it consists in pipet 0,5ml of sample into a dry 50ml beaker and add 40ml of alcoholic solvent mixture from 30% ethanol and 70% 2-propanol. This solution should be titrated with 1N NaOH solution on a titroprocessor with a combined glass-electrode filled with 1N LiCl solution in ethanol as sensor. The laboratory did not have this sensor, for this reason, in the second titration was used the same sensor as in the first one.

As it can be seen in Figure 13, sulphuric acid has two equivalence points because it is a diprotic acid. It means that yield two hydrogen ions per acid molecule and it dissociates in two stages due to one of the hydrogens is easier to remove than the other one. The first strong step in the titration curve indicated the titration end point.

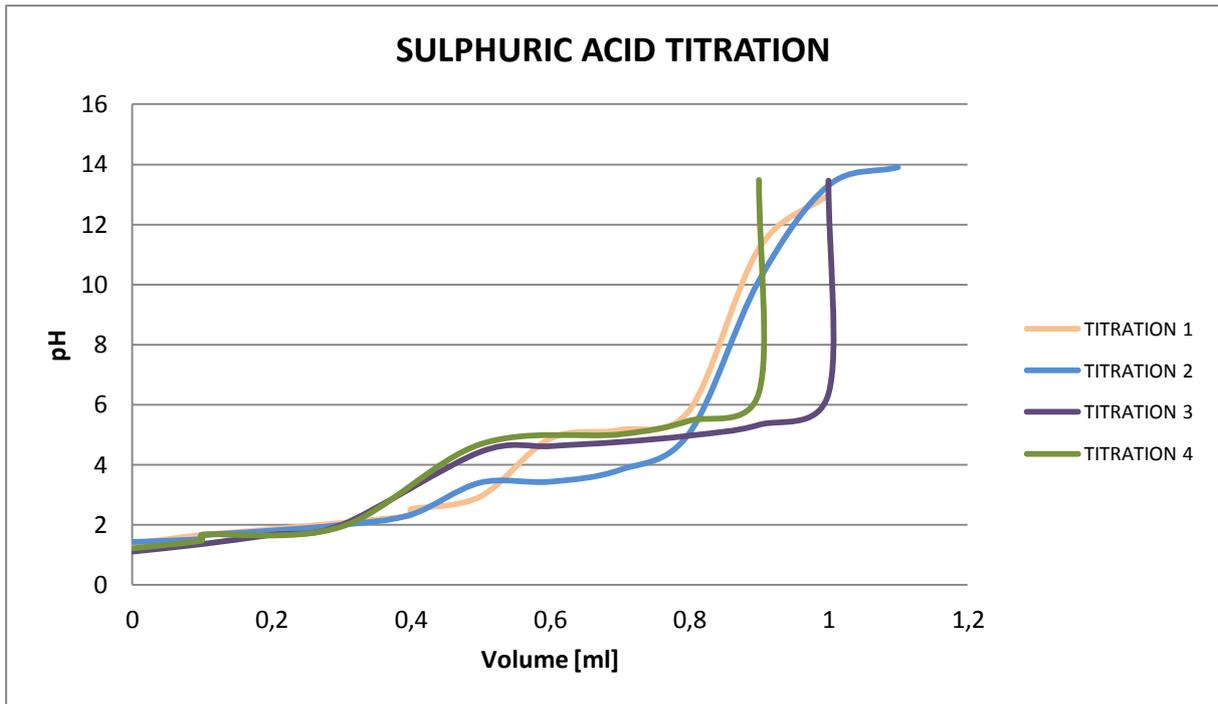


Figure 13. Sulphuric acid titration

Calculating the average consumption of NaOH solution, the amount of sulphuric acid can be calculated as shown in Equation 3.5.

$$\text{Sulphuric Acid [g/l]} = \frac{\text{titrated average volume [ml]} \cdot 49}{\text{sampling volume [ml]}} = \frac{0.45 \cdot 49}{0.5} = 44.1 \text{ g/l} \quad (3.5)$$

If the determined value of sulphuric acid is subtracted from the total acid, the amount of tartaric acid can be calculated as follows.

$$\text{Tartaric acid [g/l]} = \frac{(\text{total acid [g/l]} - \text{sulphuric acid [g/l]}) \cdot 75}{49} = \frac{(95.55 - 44.1) \cdot 75}{49} = 78.75 \text{ g/l} \quad (3.6)$$

Although the procedure followed is correct, the results obtained are not very accurate because the equipment used is not the suitable one. With the adequate tools, in a range from 20 to 60g·l⁻¹ sulphuric acid can be titrated directly with an accuracy of 5% and the tartaric acid can be calculated in a range from 40 to 120 g·l⁻¹ with an accuracy of 7% or better.

If the bath has a long service life, the analysis has to be done periodically in order to maintain the required concentrations.

3.2.2.4. Anodising process

Once the bath is manufactured and analysed, it is operative and ready for the anodising. After the pre-treatments, the tests specimens were immersed completely in the anodising tank ensuring a good connection for the current flow.

The electrolytic cycle should begin no later than 15 seconds after the immersion. As it can be seen in Figure 14, it consists in an initial potential ramp from 0 to 14V for 5 minutes whose objective is to avoid any current peak, then the voltage is maintained constant for 20 minutes and finally there is a final potential ramp from 14 to 0V for thirty seconds. The current densities obtained are between 0.6 and 1A·dm⁻². There should not be current interruptions during the cycle. Once it is finished the tests specimens should be removed from the bath as soon as possible, not later than 3 minutes after the cycle's finish.

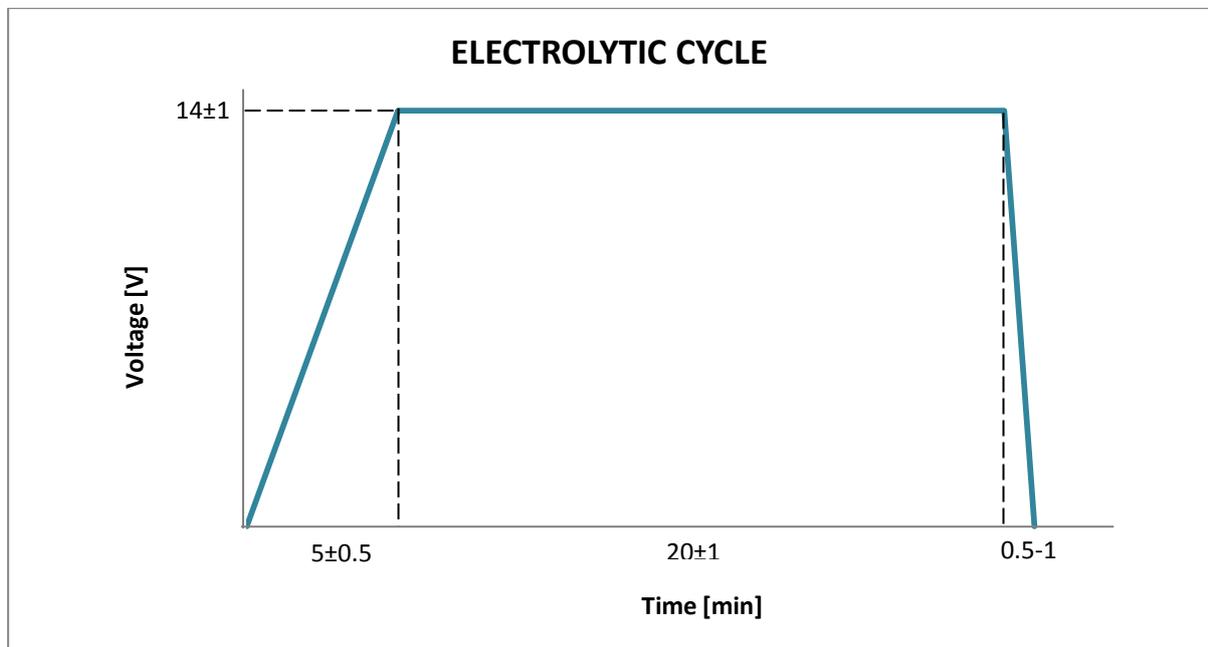


Figure 14. TSA electrolytic cycle

The rinsing process after the TSA anodising is essential because without current the electrolyte could attack the anodic film. All the samples were rinsed first with tap water and after with demineralised water for minimum 6 minutes. After this last step, they were ready for the post-treatment which are explained in the next sections.

3.2.3. Test specimen post-treatments

It is essential to have a good compatibility between the anodic film and the post-treatments. In this thesis, it is studied the performance of some current ones: sealing with hot water; sealing with a Chemical Conversion Coating (CCC), Bonderite® M-CR 1200S Aero; sealing with a Chromium VI post-treatment, potassium dichromate; and a scheme of paint, primer and topcoat, in use by Airbus. In the next sections there is a description and the main characteristics of each one.

3.2.3.1. Sealing with hot demineralised water

Sealing with hot demineralised water is used to close the pores after the anodising process. With this bath the aluminium oxide, alumina, gets hydrated becoming mono-hydrated alumina which increases in volume and closes the pores. It consists in immersing the tests specimens in demineralised hot water between 40 to 60 minutes at a temperature above or equal to 95°C.

All the samples were immersed in the tank for 40 minutes. The tank has a temperature control system that keeps it at 97±2°C. The pH has to be analysed and maintained between 5.5 and 6.5, if it is below it should be corrected adding sodium hydroxide and if it is over then it should be corrected with sulphuric acid.

After the immersion the test specimens were rinsed and finally they were dried first with compressed air and then in oven at 60°C for 20 minutes.

3.2.3.2. Sealing with Bonderite® M-CR 1200S Aero

The Bonderite® M-CR 1200S AERO, known as Bonderite® 1200S, is a Chemical Conversion Coating (CCC) manufactured by Henkel. As it can be seen in the Table 8, it is based on hexavalent chromium. It has a high level of performance in terms of corrosion resistance, thermal and electrical properties.

Component	Percentage [%]
Chromium VI oxide (CrO ₃)	30-60
Potassium tetrafluoroborate (KBF ₄)	10-30
Tripotassium hexacyanoferrate (K ₃ Fe(CN) ₆)	10-30
Sodium fluoride (NaF)	5-10
Dipotassium hexafluorozirconate (K ₂ ZrF ₆)	5-10

Table 8. Bonderite® 1200S composition

Its nominal concentration in the bath is 19 g·l⁻¹ and its maintenance values are between 15 and 22 g·l⁻¹, it does not need to be replenished often because has a long term stability. The pH must be controlled and maintained between 1.3 and 1.8, if it is below ammonium hydroxide should be added and if it is over then it should be added nitric acid.

Its operating temperature is from 21 to 30°C, for this reason the tank has a temperature control system that keeps it at 27±2°C. The bath is also equipped with an air agitation system for stirring the products. In contrast to other baths the immersion time is really short, between 0.25 seconds and 3 minutes. The samples that received this post-treatment were immersed 2 minutes.

After the Bonderite® 1200S application, the test specimens were rinsed for 6 minutes in tap and demineralised water, and dried first with compressed air and then in oven at 60°C for 20 minutes.

3.2.3.3. Sealing with potassium dichromate

Potassium dichromate is a hexavalent chromium compound which provides a high resistance to corrosion and saline conditions. Its concentration in the bath must be between 29 and 31 mg·l⁻¹ and the pH must be kept between 6 and 7.

The tank is equipped with a temperature control system that keeps it between 97 and 99°C and has an air stirring system for the agitation of the bath. The immersion time of the test specimens in this bath was 20 minutes.

After the potassium dichromate bath, the samples were rinsed for minimum 6 minutes for removing completely the product. Finally they were dried, first with compressed air and then in oven at 60°C for 20 minutes.

3.2.3.4. Paint

After the anodising and the drying, the test specimens should be painted within 24 hours and must not be exposed to adverse conditions or excessive contamination. The time can be increased to 168 hours if an ensure storage is guaranteed away of any pollution. In any case, it is better to paint the samples as soon as possible to prevent damage on the coating film. After the application of the paint, they have to be cured at room temperature for 7 days and then they are ready for performing the adhesion tests.

3.2.3.4.1. Primer

The primer, also called undercoat, is applied directly on the TSA film. The main functions of the primers are to improve the adhesion of the topcoat paint to the substrate, give more durability to the paint and protect the surface of corrosion.

The primer applied on the samples is an epoxy primer in use by Airbus, called 37035A. It has excellent adhesion properties on anodised substrates, it is resistant to aircraft hydraulic fluids and

chemicals, it is a great corrosion inhibiting and it is compatible with polyurethane, epoxy and acrylic topcoats.

It was applied on the samples using a suitable air spray gun in a controlled area because the coating quality is influenced by both the spray equipment used and the temperature, humidity and air flow of the room.

3.2.3.4.2. Topcoat

The topcoat is applied on the primers and it gives to the samples the desired finish. In this case, it was applied a polyurethane topcoat in use by Airbus too, named Aerodur Finish C 21/100 UVR. This topcoat gives to the samples mechanical strength and resistance to ultra-violet radiation and weathering, it has a high durability and flexibility and it is resistant to hydraulics fluids and chemicals.

As in the case of the primer, this polyurethane topcoat was applied on the samples by an air spray gun in a controlled area in order to obtain the required quality.

3.3. Quality tests

The quality tests performed on this thesis are the required by Airbus in order to certificate the tartaric sulphuric anodising process.

3.3.1. Coating thickness

3.3.1.1. Scope

The objective of this test is to determine the thickness of the TSA coating, see if the thickness obtained in the anodising process is the required one and if it is homogeneous on all the surface of the test specimens. To perform this test it was followed the International Standard ISO 2360, which details a non-destructive technique using eddy current instruments.

3.3.1.2. Fundamentals

The eddy current fundamental, also called Foucault current fundamental, is applied for non-conductive coatings on non-ferrous metal substrates because they are non-magnetic and good electric conductors.

The instruments based on this fundamental are equipped with a probe which generates an electromagnetic high frequency field that produces eddy current on the electric conductor where the probe is placed. This current modifies the probe's winding impedance, and this fact can be used to measure the coating thickness of the conductor. This process is shown in Figure 15.

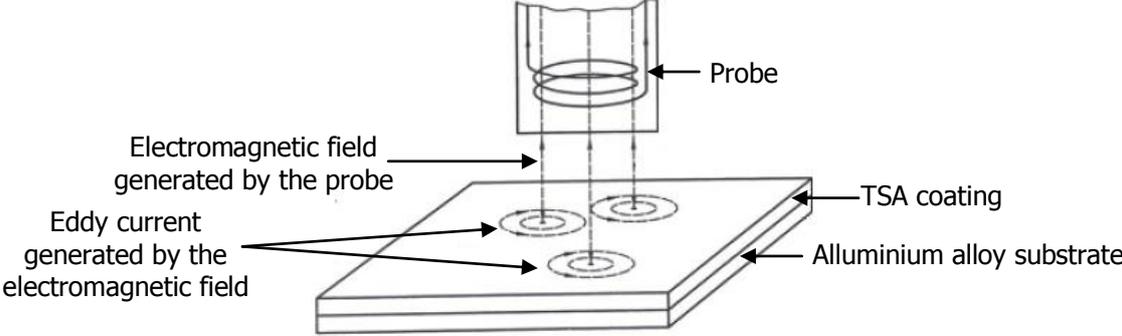


Figure 15. Scheme of the eddy current generation on the test specimens

3.3.1.3. Methodology

The measuring of the coating thickness was done using a non-destructive technique with a coating thickness instrument, specifically the Elcometer 355 which can be used in accordance with ISO 2360. It is shown in Figure 16.



Figure 16. Coating thickness gauge, Elcometer 355

The process of calculating the coating thickness is really easy using this gadget. First of all, it is necessary to calibrated it. For its calibration, it is used a suitable calibre and an appropriate probe for non-ferrous materials. The base or the zero thickness taken as a reference is the test specimen thickness without any treatment.

Once it was calibrated, 10 measurements on each specimen were done and the average value of them was taken as the coating thickness. For each different sample the Elecometer 355 had to be calibrated again because the base thickness changes. The results obtained are shown and discuss in 4.1.1.

3.3.1.4. Coating weight

3.3.1.5. Scope

The objective of this test is to determine the weight of the TSA coating film in order to check if the weight obtained is the required one and see if the anodising process was successful. For performing this test it was used the gravimetric method explained in the International Standard ISO 2106 for determining the surface density of anodic oxidation coatings.

3.3.1.6. Methodology

For the determination of the coating weight it was used a destructive technique. It consists, first of all, in cleaning the test specimens with distilled water. Then, they have to be dried for a minimum of 30 minutes at 93°C and cooled to room temperature. Once they are cooled, they are weighed using a balance sensitive to at least 10% of the anodic coating weight, in this test it was used the AG204 Mettler Toledo balance. After determining the initial weight, they have to be stripped by immersion between 5 and 6 minutes at 100°C in acid solution which composition can be seen in Table 9 .

Product	Quantity
Phosphoric acid 85%	35ml
Chromic acid	20g
Demineralised water	1000ml

Table 9. Stripping solution

After the immersion, they must be washed with demineralised water, dried and weighed. The stripping process has to be repeated until the weight of the samples remains constant which means that all the coating is removed. Finally, using the total area of the test specimen, the sum of both areas' faces, and its initial and final weight the coating weight can be calculated as follows, Equation 3.7.

$$Coating\ weight\ [mg/cm^2] = \frac{weight\ anodic\ coated\ specimen\ [mg] - weight\ stripped\ specimen\ [mg]}{specimen\ area\ [cm^2]} \quad (3.7)$$

The results obtained with this process are presented and discuss in the 4.1.2.

3.3.2. Corrosion resistance

3.3.2.1. Scope

The objective of this test is to check the corrosion resistance of the treatments applied to the test specimens, so it is used to characterize the effectiveness of their corrosion protection and to detect defects and discontinuities. To perform this test it was followed the International Standard ISO 9227 that explains the corrosion test in artificial atmospheres using salt spray.

3.3.2.2. Fundamentals

In the laboratory a way to simulate the behaviour of the materials when they are exposed to a saline atmosphere is using a salt spray chamber. It is based on spraying inside the chamber by means of compressed air a corrosive agent, in this case sodium chloride dissolve in distilled water with a concentration of $50\text{g}\cdot\text{l}^{-1}$ at 35°C .

The extremely aggressive environment produced inside the chamber lets to perform the test on an accelerated way. There is no direct correlation between the corrosion inside the chamber and the one in the real life for various reasons, but the most important ones can be summarized in three. The first one is that inside the chamber the samples' surface is always wet without any drying cycle as it happens in real life. The second one is that the temperature inside the chamber is constant at 35°C , this increases and favours the transportation of the water, the oxygen and the chloride ion compared with the external atmosphere. And the third one is that the NaCl has a concentration of 5% which is a really high value, for example, the sea water has a concentration between 1.8% and 3%.

However, this test is widely used in industry for its simplicity and because it gives an accurate idea of the corrosion resistance of the coatings checking the time taken for oxides to appear. If the coatings are able to resist the aggressive conditions inside the chamber, they will be able to resist the subsequent service environment.

3.3.2.3. Methodology

After the application of the inorganic coatings and a day of cure the test specimens are placed inside a salt spray chamber. In this case, the salt spray chamber used was the Ascott S1000t which can be seen in Figure 17.



Figure 17. Salt spray chamber Ascott S1000t and NaCl solution tank

First of all, before positioning the samples inside it, they have to be clean with demineralised water. Once they are clean they are placed on the supports. Their position in the chamber is very important. They must be facing upwards at an angle of 20 degrees to the vertical, parallel to the flow. There cannot be contact between the different specimens or with other metal surfaces. The supports and all the chamber's materials have to resist corrosion in order to not interfere with the results of the tests. In Figure 18 it can be seen the salt spray chamber interior.



Figure 18. Supports of the spray salt chamber

The duration of the test inside the chamber depends on the treatment that is applied to the specimen. In order to detect any start of corrosion on the specimens, it was performed a daily inspection. During this inspection it was collected a sample of NaCl solution for its analysis because the pH must be controlled and kept between 6.5 and 7.2.

Once completed the test, the specimens must be removed from the salt spray chamber and washed with demineralised water in order to eliminate the salt that is left on the surface after the test. Finally, the corrosion degree on the specimens has to be evaluated to confirm if they pass the test or not.

3.3.3. Paint adhesion

3.3.3.1. Scope

The objective of this test is to check the compatibility and the good adhesion between the anodic TSA film and the paint. Two tests were performed, the dry and the wet adhesion tests. They were performed on samples with only primer was applied and on samples with primer plus topcoat were applied. In both cases, the test procedure followed was the same: the international standard ISO 2409.

3.3.3.2. Methodology

3.3.3.2.1. Dry adhesion test

After the cure period the samples are ready for the dry adhesion test. It consists in making a grid of six cuts in each direction. Depending on the thickness of the coating and on the type of the substrate the spacing between the cuts varies, for hard substrates like the aluminium and for a thickness up to 60 μm the spacing must be 1mm. For making the grid, it is used the tool than can be seen in Figure 19, the Erichsen Multi Cross Cutter Model 295. It is very important that the cuts reach the substrate for performing well the adhesion test.



Figure 19. Erichsen Multi Cross Cutter Model 295

Once the grid is done, the specimen's surface is clean with a brush to remove the paint that is extracted by the cuts. Then, the tape is positioned as shown in Figure 20 and is removed with a single movement with an angle as close as possible to 60°.

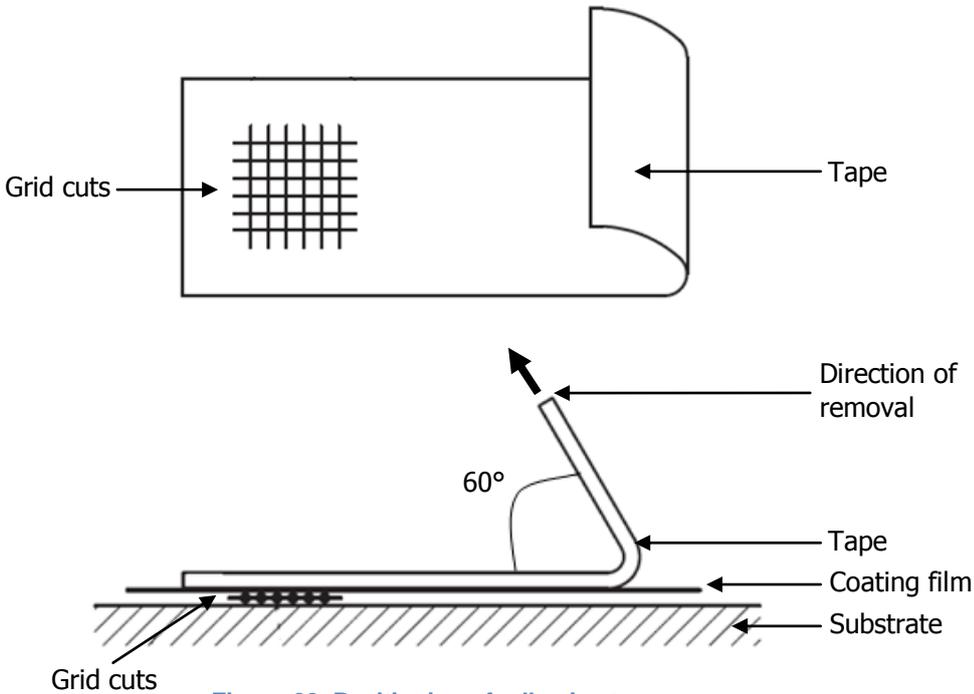


Figure 20. Positioning of adhesive tape

3.3.3.2.2. Wet adhesion test

After the cure period, in order to perform the wet adhesion test the samples have to be immersed in demineralised water for 14 days at 23±2°C. The laboratory has a controlled environment, where the temperature and the humidity are regulated, for this reason the samples were left at room temperature inside it.

When the samples are removed from the immersion bath after 14 days, they have to be dried with paper. Then it is performed the test described in the previous section within 10 minutes after their removal from the demineralised water. As explained above, it consists in cutting the grid and then positioning the tape for its removal with a single movement.

3.3.4. Dye spot test

3.3.4.1. Scope

This test was performed on the specimens which received as a post-treatment the potassium dichromate. Its objective is to determine the quality of this post-treatment checking the degree of sealing verifying the absorption loss of the samples after its application.

3.3.4.2. Fundamentals

Once the post-treatment of potassium dichromate is applied on the specimens the surface is sealed, for this reason, if it is obtained a uniform coating and its application is successful the surface loses the absorption power. So, when it is poured on the samples few drops of dye, the surface does not absorb it and the coloration remaining on the surface is very light.

3.3.4.3. Methodology

The procedure to perform this test is very simple. First of all, the test specimens have to be cleaned using a suitable organic solvent, in this case it was used acetone. Then, with a ruler and a pencil is drawn on the specimens a square of approximately 1 cm². Inside the square it is poured a few drops of dye Sanodal Blue 2LW which concentration must be 5 g·l⁻¹. In Figure 21 it is shown a sample of each alloy after drawing the square and the application of the dye. The sample I, II and III are the alloys 7175, 2024 and 6061 respectively. After 5 minutes, the surface has to be washed using water and a neutral soap for removing the dye. Finally, the samples have to be dry and the coloration obtained can be evaluated.

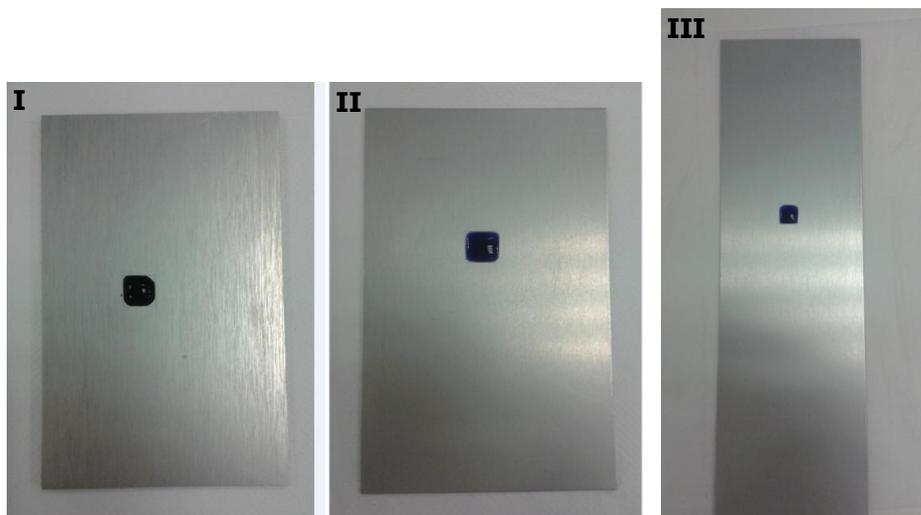


Figure 21. Application of the Sanodal G on the samples: (I) Alloy 7175, (II) Alloy 2024 and (III) Alloy 6061

3.3.5. Dye spot test with prior acid treatment

3.3.5.1. Scope

The objective of this test is to determine the quality of the anodic coatings checking their loss of absorptive power after the sealing with hot water, in this case, it is verified the quality of the TSA anodic coating. The test was performed following the International Standard ISO 2143.

3.3.5.2. Fundamentals

During the immersion inside the bath with hot water the pores that were open during the anodising are closed, and the surface of the test specimens remains completely sealed. Therefore, if the anodising and the sealing process have succeeded when it is applied on the surface a dye drop, the colour remaining is very light because the surface repels it.

3.3.5.3. Methodology

First of all, the surface of the samples has to be cleaned and it is drawn on them with a ruler and a pencil a square of approximately 1 cm^2 . Then it is necessary to prepare the acid solution composed of $25 \text{ ml}\cdot\text{l}^{-1}$ sulphuric acid and $10 \text{ g}\cdot\text{l}^{-1}$ potassium fluoride. Once the solution has been prepared, a spot is applied inside the drawn square for 1 minute. After that, the surface has to be washed off and dried.

The next step after the application of the acid solution is to apply inside the square a drop of dye for one minute, in this case it was applied $5 \text{ g}\cdot\text{l}^{-1}$ Sanodal Blue 2LW. Finally, the dye spot is washed off with a mild abrasive soap and the coloration remaining on the specimen can be evaluated.

4. Results

4.1. Quality of the TSA anodic film

In this section the quality of the TSA anodic film is analysed based on the results got from the quality tests explained in the previous sections.

The tests were performed on three different alloys: AA2024, AA7175 and AA6061. The preparation procedure followed was the same for each one. They were immersed in the pre-degreasing, the degreasing, the acid etching and the anodising bath. As the objective of this section is to study the TSA coating quality, after these baths, the test specimens did not receive any post-treatment. Only for the performance of the corrosion and dye spot tests the samples were immersed in the sealing tank of hot demineralised water in order to close the pores of the TSA film.

With the performance of these tests three different parameters are compared and studied. First of all, if there is a significant difference between the coating films obtained on the three different alloys, or otherwise, if the results obtained are similar regardless its composition and its thermal treatment.

Also it is analysed if the etching bath has influence on the final results. It is verified if the new etching bath without chromium compromises the effectiveness of the anodising process and it is confirmed if the same results are achieved with both of them.

And the last analysis done is the comparison between the results obtained with the TSA anodising and those obtained with the CAA anodising, to see if the first process is really a good substitute for the second one.

In order to compare the efficiency of the Bonderite® Smutgo NCB, Bath 2, with the current etching bath with chromium, Bath 1, the tests were performed for each alloy on two samples: one was immersed in the first bath and the other in the second one.

All the information and values related with the CAA anodising tests were provided by the chemical laboratory at OGMA. They have to perform monthly tests in order to ensure the quality of their surface treatments. The results presented in the next sections correspond to the quality control tests of February. However, the comparison between the CAA and the TSA processes is only performed for the AA2024 and AA7175. This is because they are the only representative alloys of its production right now, so, they do not need to perform tests on the AA6061.

4.1.1. TSA coating thickness

The TSA coating thickness was determined using the Elecometer 355 and following the procedure explained in section 3.3.1. In Table 10 there are the results obtained, ten measurements of thickness were made on different parts of the test specimens and the average value of them was taken as the TSA coating thickness of the sample.

Test specimen		Thickness [μm]										Standard deviation [μm]	Average thickness [μm]
Material	Acid etching												
AA2024	Bath 1	4.3	4.1	3.1	5.4	4.1	4.4	5.2	2.9	3.4	3.4	0.84	4.0
AA2024	Bath 2	2.9	3.5	3.6	3.8	3.3	3.1	3.7	2.9	2.8	3.4	0.36	3.3
AA7175	Bath 1	3.5	3.1	3.2	3.2	3.9	3.1	2.3	2.9	3.7	3.5	0.45	3.2
AA7175	Bath 2	5.1	4.5	4.4	3.9	3.8	3.9	4.1	4.2	3.7	4.3	0.41	4.2
AA6061	Bath 1	3.5	3.8	3.6	4.1	3.2	3.1	3.9	3.8	3.7	3.8	0.31	3.7
AA6061	Bath 2	2.8	2.1	3.5	3.3	4.4	2.9	2.7	4.4	3.1	2.4	0.77	3.2

Table 10. TSA coating thickness

There are different factors that could have affected the thickness measurements presented above and they have to be taken into account in the analysis of the results. The first one is the edge effects. At the edge of the samples the magnetic field is obstructed unless the instrument is correctly regulated, for this reason it has avoided performing measurements there. The curvature and the roughness of the surface can affect the measurements, too. In this case the curvature is not a problem because the samples do not have it, but the roughness can produce both random and systematic errors. For reducing the first error, it is necessary to make multiple measurements, in this case ten are considered enough, and for avoiding the second one the calibration has been done on a base metal with an equivalent roughness of the sample to be measured. The position of the probe it is also fundamental. It must be placed tilt and directly on the sample, if not the gap between the sample and the probe can introduce an extra thickness. The pressure made on the probe during the measurements and the calibration must be constant, if not it can produce errors too. The temperature can affect the characteristics of the probe, for this reason, it is important that the calibration and the measurements take place in the same conditions. And finally, an external electromagnetic field can influence in the measurements, so they have to be made far away of interfering fields. All the measurements shown in Table 10 were made taking into account all the factors mentioned above.

Comparing the ten measurements made on each test specimen it can be seen that they are similar along the entire surface. This means that the TSA film is homogeneous and there are not areas without anodised.

The coating thicknesses obtained in each alloy are not only homogeneous but also satisfactory. The thickness must be between 2 and 7 μm and they are around 3 and 4 μm . Also it can be seen that they are similar, so, the TSA thickness film produced during the anodising process is not influenced by the composition or the heat treatment of any alloy tested.

Analysing the thicknesses obtained in the same alloy but using a different etching bath, it cannot find any significant differences in the results either. In the case of the AA2024 and AA6061 alloys, using the Bonderite® Smutgo NCB the average thickness obtained is slightly smaller than using the first bath, but their variation is not significant.

In the next tables, Table 11 and Table 12, there are the thicknesses obtained with the CAA process provided by the chemical laboratory at OGMA. In Table 11 there are the coatings thicknesses of 4 different test specimens of the alloy AA7175 and in Table 12 there are the coating thickness of 4 different samples of the alloy AA2024.

Material	Test specimens thickness [µm]			
AA7175	2.8	2.9	5.4	4.2

Table 11. CAA coating thickness of the alloy 7175

Material	Test specimens thickness [µm]			
AA2024	3.7	3.9	3.9	4.5

Table 12. CAA coating thickness of the alloy 2024

The CAA coating thickness of the alloy AA7175 vary between 2.8 and 5.4 µm. If these values are compared with the TSA anodising results it can be seen that they are similar, specially they are 3.2 and 4.2 µm.

In the case of the alloy AA2024, the variation of the CAA coating thicknesses is smaller. They are between 3.7 and 4.5 µm. Comparing them with the TSA results it can be checked that they are almost identical, since the TSA coating thickness obtained are 4.0 and 3.3 µm.

So, in terms of coating thickness it can be confirmed that the results obtained with the TSA anodising are equivalent to those obtained with the CAA anodising.

4.1.2. TSA coating weight

The coating weight of each sample was calculated following the procedure explained in the section 3.3.1.4. As it can be seen in the Table 13, two different iterations were sufficient to remove all the anodic coating film from the samples. It was considered that the weight remained constant when only the last or the two last decimals varied between iterations. The results obtained are shown in the Table 13.

Test specimen		Initial weight [g]	Final weight [g]		Area [cm ²]	Coating weight [mg·dm ⁻²]
Material	Acid etching		Iteration 1	Iteration 2		
AA2024	Bath 1	108.2617	108.1451	108.1445	200	58.6
AA2024	Bath 2	109.2093	109.1021	109.1019	200	53.7
AA7175	Bath 1	115.7595	115.6477	115.6462	200	56.65
AA7175	Bath 2	114.8365	114.7186	114.7143	200	61.1
AA6061	Bath 1	42.0495	41.8346	41.8324	375	57.89
AA6061	Bath 2	43.3203	43.0885	43.0883	375	61.86

Table 13. TSA coating weight

The coating weight obtained must be higher than 22 mg·dm⁻², so it can be seen analysing the results that they are satisfactory in all the alloys. There is no significant difference between the coatings weights obtained on them. Regardless the composition and the thermal treatment of the alloys tested, all three have very similar values.

For the alloys AA7175 and AA6061, the coating weights obtained are slightly higher using as an acid etching the second bath than using the first one. As opposite to that, in the case of AA6061 the coating weight of the sample immersed in the first bath is larger than the one immersed in the second one. However, the variation between them is not significant.

In Table 14 there are the results obtained from the test specimens anodised with the CAA bath. There are three samples of the alloy AA7175 and three more of the alloy AA2024. It is shown only the initial and the final weights without intermediate iterations.

Material	Initial weight [g]	Final weight [g]	Coating weight [mg·dm ⁻²]
AA7175	118.1632	118.0412	59.74
AA7175	114.2082	114.0864	59.63
AA7175	117.9502	117.8275	60.17
AA2024	35.6099	35.5010	53.39
AA2024	35.5321	35.4233	53.28
AA2024	35.5861	35.4755	54.14

Table 14. CAA coating weight

As it can be seen, for the three samples of the same alloy the CAA coating weight obtained is similar, in the case of the alloy AA7175 is around 59 mg·dm⁻² and for the alloy AA2024 is about 53 mg·dm⁻². Comparing these values with the TSA results it is shown that the coating weights are almost equal, specially for the alloy AA7175 are 56 and 61 mg·dm⁻² and for the alloy AA2024 are 58 and 53 mg·dm⁻².

4.1.3. TSA coating corrosion resistance

The TSA film generated during the anodising process has two main functions: the first one is to give protection to the aluminium alloy against corrosion and the second one is to act as a link between the alloy and the possible post-treatment. With the performance of this test, it is verified if the TSA film meets the first requirement: to give the required corrosion protection.

After the sealing in hot demineralised water, as in the case of the CAA film, it is considered that the TSA film gives a good protection against corrosion when at least it can protect the aluminium alloys for 96 hours inside the salt spray chamber. After this period, on the samples surfaces cannot appear any irregular dark grey area such as marks, streaks or spots. It can have at most 2 pits·dm⁻² and any of them can exceed 0.8 mm in diameter.

In Figure 22 there are the results obtained in the first attempt of performing the test. It was performed on six samples, two of each alloy. In order to verify the efficiency of the Bonderite® Smutgo NCB and to demonstrate that the same results are obtained with both acid etching baths, one sample of each alloy was immersed in the first bath and the other sample was submerged in the second one.

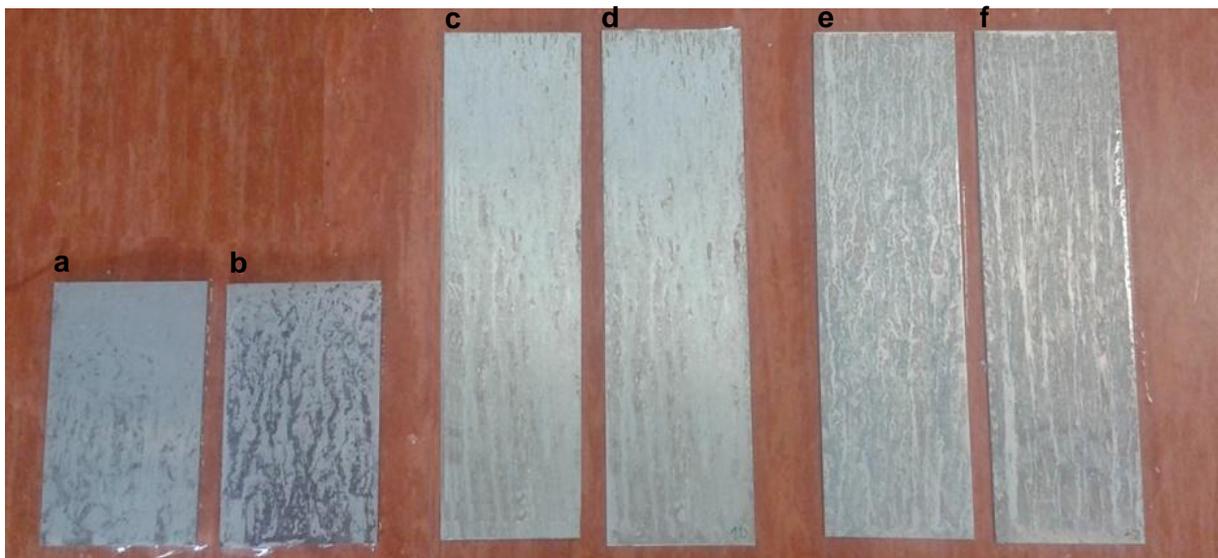


Figure 22. Sealing with hot water corrosion test: (a) Alloy 7175 etching with Bonderite® Smutgo NCB, (b) Alloy 7175 etching with the first bath, (c) Alloy 6061 etching with Bonderite® Smutgo NCB, (d) Alloy 6061 etching with the first bath, (e) Alloy 2024 etching with Bonderite® Smutgo NCB and (f) Alloy 2024 etching with the first bath

As it can be seen in Figure 22, the samples did not pass the corrosion test. The corrosion started to appear on all of them after only 24 hours inside the salt spray chamber and after 96 hours of exposure all the specimens had a high level of corrosion on the entire surface. The results obtained are completely unexpected. TSA film was not able to protect any of the alloys tested, regardless of the composition and the heat treatment received

After analysing the different factors that could have generated this negative result, it was deduced that the problem did not lie in the etching bath, because corrosion appeared on both samples, on the samples immersed in the first acid etching bath and on the samples immersed in the second one. It was concluded that the problem could lie in the sealing bath of hot water. As explained in previous sections, this bath requires a periodic analysis in order to control and maintain the pH between 5.5 and 6.5. When the pH is below it should be corrected with sodium hydroxide and if it is over then it should be added sulphuric acid. Even so, the service life of the bath is not unlimited and also needs to be renovated. At the time of the test, the bath was not in use, so, it could be that it was contaminated or some parameter was out of range.

For this reason, the test was repeated after the renewal and analysis of the bath. It was performed on one sample of each alloy and the acid etching bath used was the Bonderite® Smutgo NCB. As it can be seen in Figure 23, the results obtained with the repetition of the test after the renovation of the bath are completely satisfactory. The TSA film was able to protect the samples really well and corrosion did not appear on any of them.

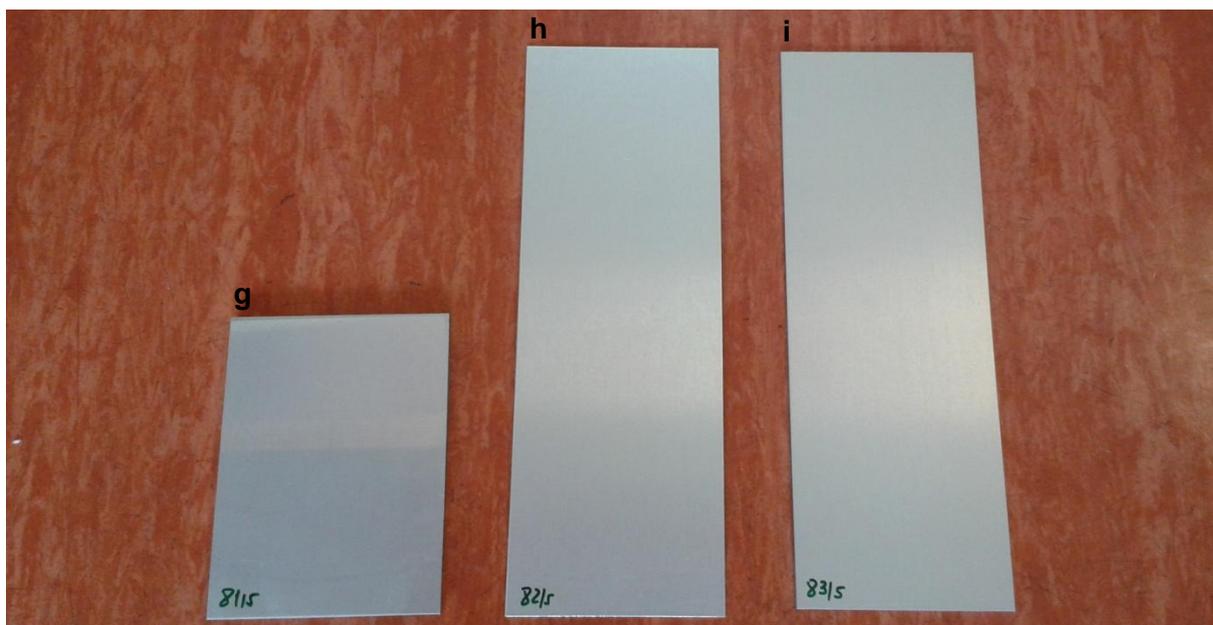


Figure 23. Sealing with hot water corrosion test repetition: (g) Alloy 7175, (h) Alloy 6061 and (i) Alloy 2024

After the performance of this test it is possible to draw some significant conclusions. First of all, the importance of analysing and controlling the baths, and when it is necessary renew them, in order to get the required quality. The test demonstrates that the TSA film is able to give the same corrosion protection than the CAA film. It is verified its compatibility with the three alloys tested, regardless of the composition and the heat treatment received. And also it is checked that the results obtained using the Bonderite® Smutgo NCB are excellent, so, in this case it appears to be a good substitute for the acid etching bath with sodium dichromate.

4.1.4. TSA coating degree of sealing

The degree of sealing of the TSA coating is evaluated checking its resistance to a dye spot test with a prior acid treatment. This test was performed on six samples, two of each alloy, after the sealing with hot water. As explained in previous sections, this test evaluates the loss of absorptive power of the anodic coatings.

After the performance of the test, following the procedure described in section 3.3.5, the results obtained have to be evaluated comparing the coloration remaining on the sample with the coloration shown in Table 15. It is considered that the specimens have lost their power of absorption and have passed the test when the remaining intensity colour is comparable to the 0, 1, or 2 intensities.

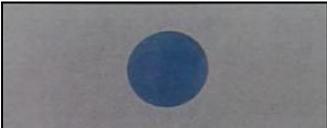
Sanodal Blue	Intensity	Loss of absorptive power
	5	Null
	4	Very weak
	3	Weak
	2	Average
	1	Strong
	0	Total

Table 15. Possible degrees of coloration

The results obtained after the performance of the test are presented in Figure 24 and Figure 25. The samples j and k correspond to the alloy AA2024, the specimens l and m are AA7175 samples and the last two specimens, n and o, correspond to the alloy AA6061. The first sample of each group was immersed in the Bonderite® Smutgo NCB bath, and the second was submerged in the first acid etching bath.

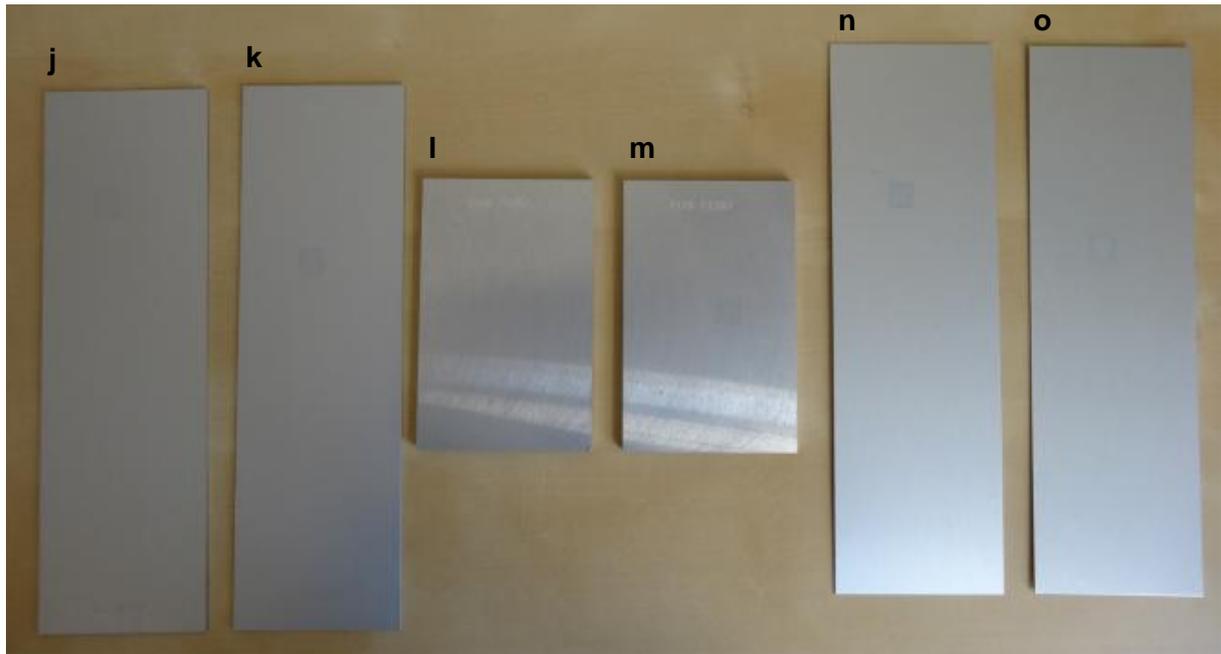


Figure 24. Sealing with hot water dye spot test: (j) Alloy 2024 etching with Bonderite® Smutgo NCB, (k) Alloy 2024 etching with the first bath, (l) Alloy 7175 etching with Bonderite® Smutgo NCB, (m) Alloy 7175 etching with the first bath, (n) Alloy 6061 etching with Bonderite® Smutgo NCB and (o) Alloy 6061 etching with the first bath

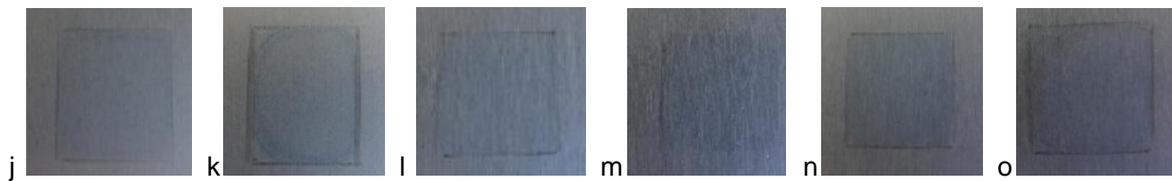


Figure 25. Sealing with hot water dye spot test expansion

As it can be seen in the previous figures, the coloration remaining on all the samples is very light and it corresponds to intensity 1. It can be concluded that all of them present a high loss of absorptive power.

On all the alloys tested, regardless of the chemical composition and the heat treatment, is achieved a good degree of sealing able to repel the dye spot. The results obtained are satisfactory with both, the samples immersed in the first etching bath and the ones immersed in Bonderite® Smutgo NCB, so, once again this product seems to be a good non-chromate substitute for the current acid etching bath.

4.2. Quality of the post-treatments

In this section it is studied and analysed the compatibility of the TSA coating film with the different post-treatments. One of the TSA film main functions is to provide and facilitate a good adhesion between the aluminium alloy and them, for this reason it is fundamental to check if exists a perfect link between both and if they provide a good protection to the alloy.

Depending on the post-treatment it was performed different types of tests in order to check its quality. For the potassium dichromate it was performed two tests: it was checked its corrosion resistance and its loss of absorptive power. In the case of the test specimens with Bonderite® 1200S it was performed only the corrosion resistance test. And for the painted samples it was analysed the dry and wet adhesion achieved.

4.2.1. Post-treatments corrosion resistance

4.2.1.1. Sealing with potassium dichromate

The samples sealed with potassium dichromate were placed inside the saline chamber after one day of cure. This treatment is considered to give a good corrosion resistance when after 336 hours of exposure the samples show less than 2 pits·dm⁻² and any of them exceed 0.8 mm in diameter. On the test specimen surface cannot be any irregular dark grey areas such as spots, streaks or marks.

In order to perform the test the samples were placed inside the saline chamber with an inclination of 20 degrees from the vertical. Although the total duration of the test was 336 hours, it was carried out daily inspections to detect the start of any appearance of corrosion during the test.

In the following two figures, Figure 26 and Figure 27, can be seen the samples after performing the test. In the first one, there are the six samples immersed in the etching bath with chromium and in the second one there are the samples which received the acid etching with Bonderite® Smutgo NCB.

The first two samples of each figure, group A and group D, correspond to the alloy AA2024. The second groups, group B and E, are samples of the alloy AA7175. And the last two groups of each figure, group C and F, correspond to the alloy AA6061.

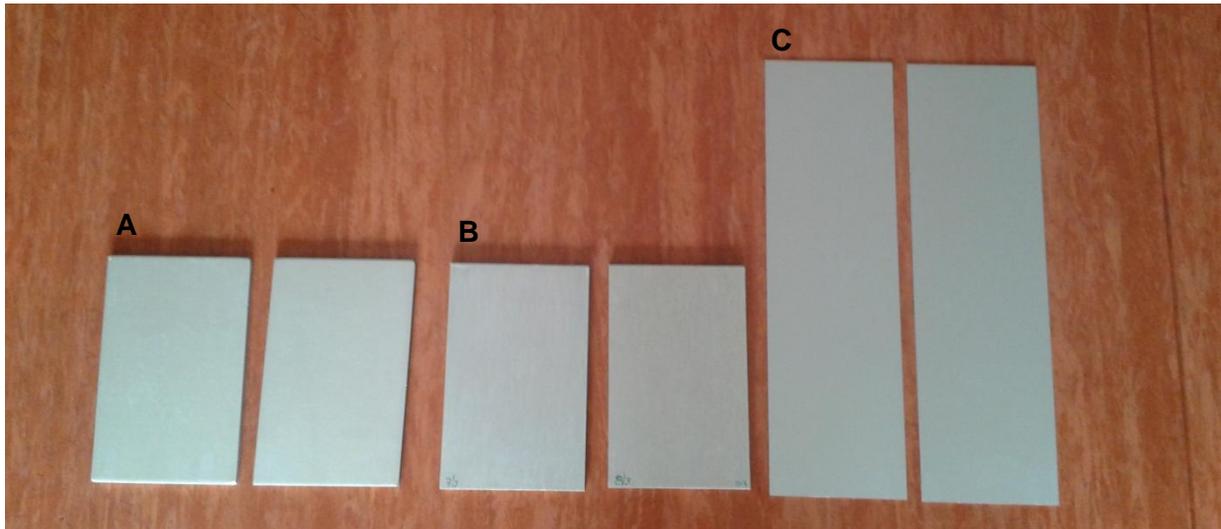


Figure 26. Potassium dichromate corrosion test with etching bath 1: (A) Alloy 2024, (B) Alloy 7175 and (C) Alloy 6061

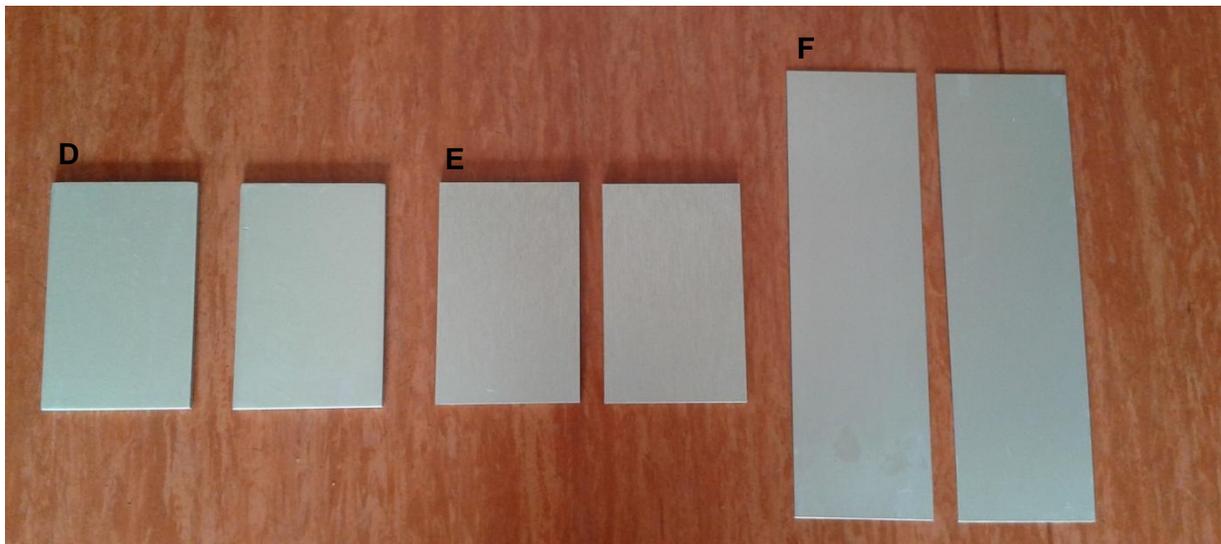


Figure 27. Potassium dichromate corrosion test with etching bath 2: (D) Alloy 2024, (E) Alloy 7175 and (F) Alloy 6061

As it can be seen the results obtained are completely satisfactory because after 336 hours of test there is no evidence of corrosion on any of the test specimens. It can be concluded that the potassium dichromate is completely compatible with the coating film produced in the TSA anodising bath in the case of all the alloys tested and confirm that their combination provide the corrosion resistance required.

Comparing the test specimens immersed in the two different acid etching baths, it can also be affirmed that using the Bonderite® Smutgo NCB the results achieved in terms of corrosion resistance are equivalent to those obtained with the etching bath with chromium.

4.2.1.2. Sealing with Bonderite® M-CR 1200S Aero

The Bonderite® M-CR 1200C Aero is a chemical conversion coating that normally is applied directly on the bare surface to increase and protect the aluminium from corrosion and to provide a good link between the metal and the organic coating.

As it mentioned above, although one of its main components is chromium VI it presents some advantages respect to the potassium dichromate as a post-treatment. The Bonderite® 1200S has a shorter period of immersion, only between 1 and 3 minutes. It means that the exposure time to the chromates is reduced too. Another advantage is that it does not need a temperature control because it works a room temperature. The potassium dichromate works at higher temperatures so its bath has more vapour emissions than the Bonderite® 1200S bath. For these reasons it was considered interesting to see if there is compatibility between this product and the TSA film and check if it is achieved the some corrosion resistance with both products.

As in the case of the potassium dichromate, the test was performed on twelve specimens, six of them were immersed in the first etching bath and the other six in the second one. The results after 336 hours inside the salt spray chamber are shown in Figure 28 and Figure 29. The first group of two samples in each figure, group G and J, corresponds to the alloy AA2024. The second groups, group H and K, are AA7175 samples. And the last two groups of two specimens each, group I and L, corresponds to the AA6061.

The requirements to consider that a good corrosion resistance is obtained are the same of the above section. After 336 hours of exposure inside the salt spray chamber the samples have to show less than 2 pits·dm⁻² and any of them can exceed 0.8 mm in diameter. And on the test specimen superficies cannot be any irregular dark grey areas such as spots, streaks or marks.

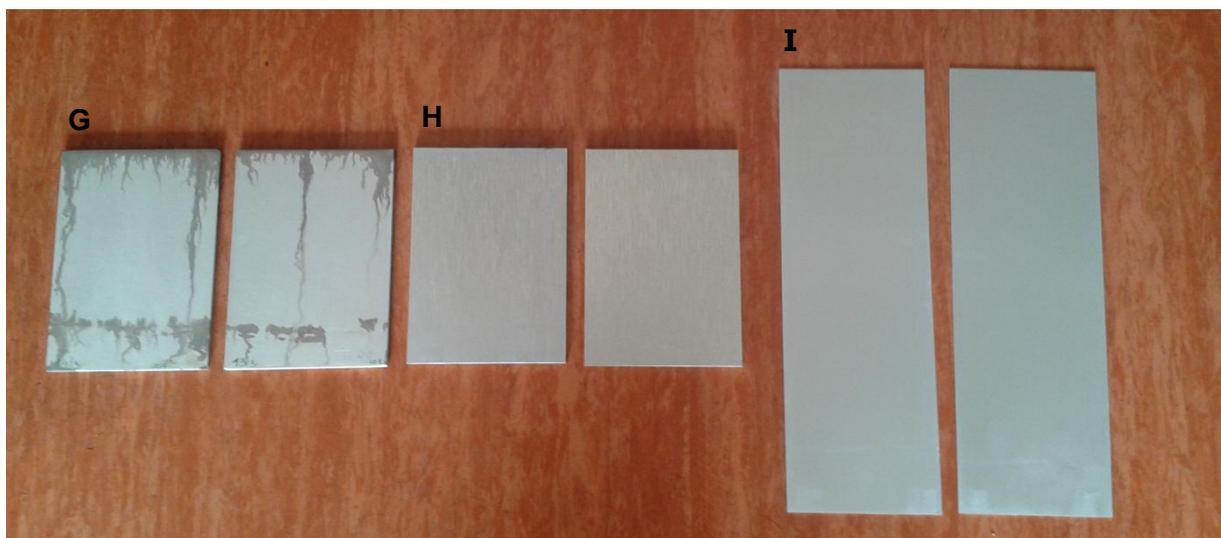


Figure 28. Bonderite® 1200S corrosion test with etching bath 1: (G) Alloy 2024, (H) Alloy 7175 and (I) Alloy 6061

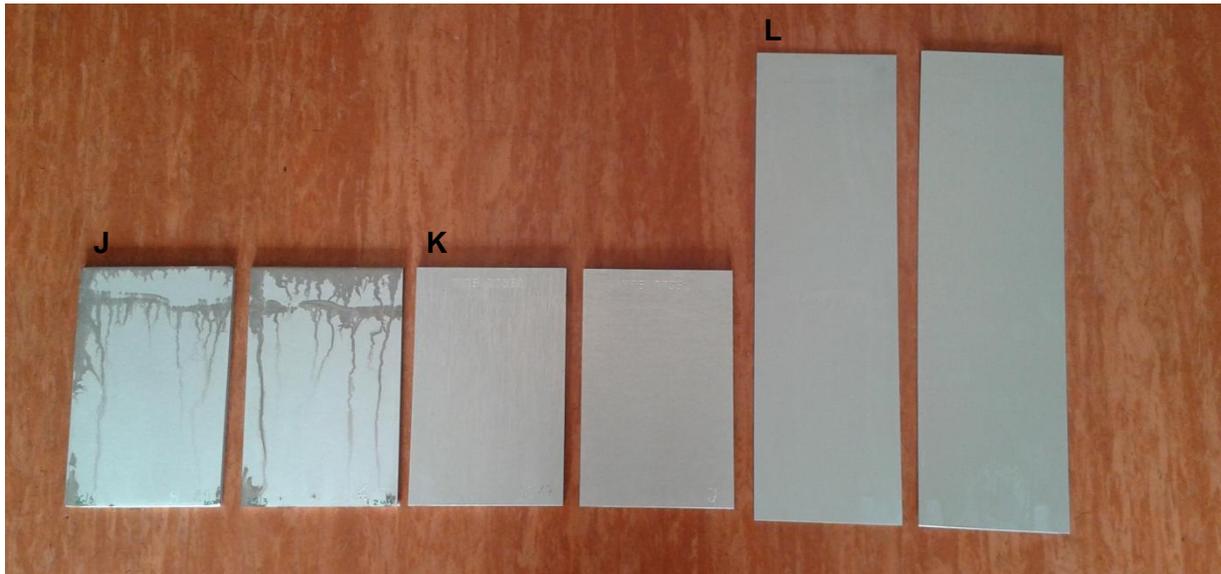


Figure 29. Bonderite® 1200S corrosion test with etching bath 2: (J) Alloy 2024, (K) Alloy 7175 and (L) Alloy 6061

As it can be seen in the above figures, on the alloys AA7175 and AA6061 has not appeared any corrosion, so they have passed the test successfully. There is a really good compatibility between the TSA film and the Bonderite® 1200S on them, and as a result, these treatments give a very good protection. In the case of these alloys the same satisfactory results are achieved with both etching baths, so once again, the Bonderite® Smutgo NCB appears to be a good substitute for the acid etching bath with sodium dichromate.

In the case of the alloy AA2024, the results are completely different and it has not passed the corrosion resistance test. Corrosion began to appear after only 144 hours inside the salt spray chamber, and as it can be seen, the samples have a high grade of corrosion after 336 hours of exposure.

The corrosion has appeared on both samples, on the samples immersed in the first acid etching bath and on the samples immersed in the second one. Therefore, it can be concluded that the problem is not related with the new acid etching product.

Analysing where corrosion appeared it can be seen that it is located near the edges of the specimens and on the area where the wire was tied in order to connect the samples with the anodic bar of the tank.

Based on the results obtained in the first test, the experience was repeated modifying different parameters in order to see their influence on the final results and check if it was possible to achieve an improvement with any of them on the AA2024.

First of all, in order to eliminate the corrosion originated on the samples where the wire was placed, it was tested an alternative method of subsection. Because of the small dimensions of the anodising tank and the need of a good connection for the current flow during this process, in the TSA bath it was used the wire but in the other baths the samples were immersed using a titanium rack. In Figure 30 it is shown the both different fastening methods used: the titanium rack and the wire.

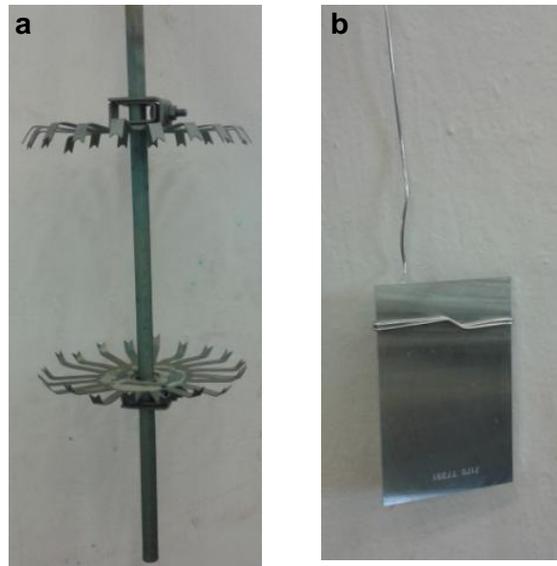


Figure 30. Fastening methods: (a) titanium rack and (b) wire

Apart from the areas in direct contact with the wire, the corrosion also started to appear at the edges of the samples, for this reason, it was tried to isolate all of them with adhesive tape.

It was also studied the influence of the drying process. It was compared the results obtained in the case of drying the sample with only compressed air and in the case of drying the specimen first with compressed air and then in oven at 60°C for a longer time, 40 minutes.

The last parameter analysed was the immersion time in the Bonderite® 1200S bath. It was checked if increasing the immersion time from 2 to 3 minutes the results obtained were better than the previous ones.

Figure 31 shows the four samples after the corrosion test modifying the different parameters. The specimen O followed the same process as the previous ones but it was immersed with the titanium rack instead of using the wire. The specimen P was immersed with the titanium rack too and it was immersed in the Bonderite® 1200S tank for 3 minutes instead of 2.

The samples M and N were immersed with the titanium rack and have their edges isolated with adhesive tape, both were immersed for 2 minutes but the sample M was dried with compressed air and in oven and the other one only with compressed air.

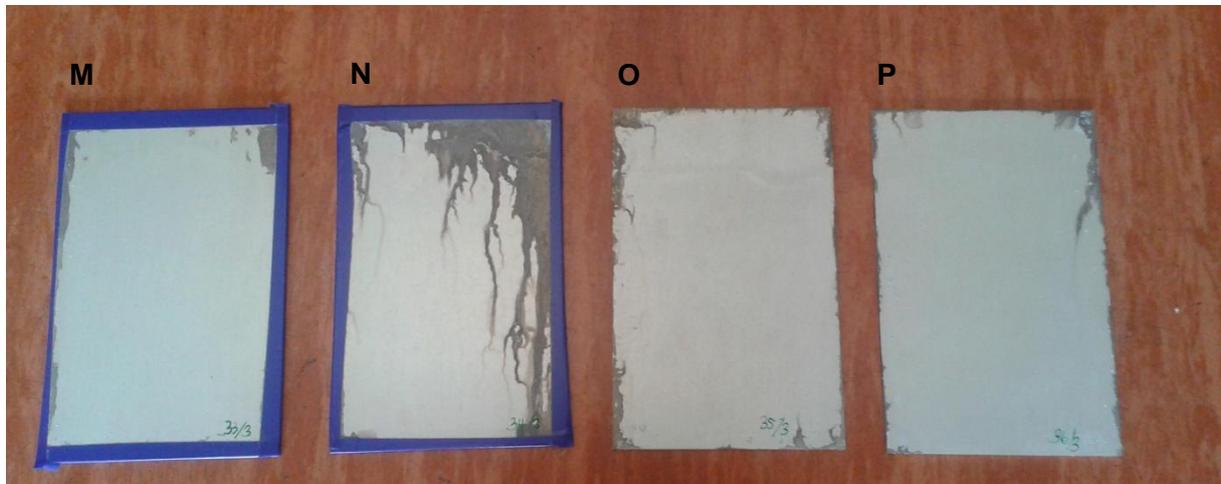


Figure 31. Bonderite® 1200S corrosion test repetition on the Alloy 2024

Analysing the results, it can be observed that it has been possible to eliminate the corrosion produced near the areas where the wire was, using the titanium rack instead of the wire during the immersions inside the baths.

Comparing the samples O and P, it is deduced that the increase of time inside the Bonderite® 1200S bath does not improve the corrosion resistance of the specimens, because both of them show the same level of corrosion.

Studying the results obtained on the samples M and N, it is noticed the importance of drying the specimens in oven and not only with compressed air. The specimen N which was dried only with compressed air shows a very high degree of corrosion compared to the other one.

Also it can be seen on the specimen M that isolating the edges of the specimens does not eliminate the appearance of the corrosion on these areas. Although there is a decrease, it is not enough to pass the test.

This negative result on the alloy AA2024 could be related to its composition. According to the investigations performed by García Rubio [15] the morphology of the anodic film depends on the alloy. If it has a high copper alloying element, as in the case of the AA2024, the anodic film presents distorted porous, whereas if the containing is lower present organised films. The corrosion resistance is also affected for the alloy composition. Anodic films with high copper tend to degradation whereas those with low copper content present a better sealing.

After the analysis performed it can be concluded that the Bonderite® 1200S as a post-treatment is compatible with the TSA anodising in the case of the alloys AA7175 and AA6061. In the case of AA2024, although it has been possible to reduce the initial corrosion, it has not been entirely eliminated and has not passed the corrosion test.

4.2.2. Post-treatments dye spot resistance

4.2.2.1. Sealing with potassium dichromate

This test was performed on samples sealed with potassium dichromate. The objective of this test is to check the sealing quality of this post-treatment on the TSA anodic film. In order to verify their affinity and see if the samples are well sealed this test analyses the loss of absorptive power.

As in the case of sealing with hot water, the results obtained are evaluated comparing the coloration remaining on the sample with the coloration shown in Table 15. The specimens have lost their power of absorption and have passed the test when the remaining intensity colour is comparable to the 0, 1, or 2 intensities.

In total the test was carried out on six test specimens, two of each alloy. One of them was immersed in the Bonderite® Smutgo NCB bath for the acid etching process and the other one was immersed in the first bath. So, it is possible to check and compare if there is a good sealing on the different alloys and if the some results are achieved using both acid etching baths.

The results obtained are shown in Figure 32. The samples Q and R correspond to the alloy AA2024, the specimens S and T are AA7175 samples and the last two specimens, U and V, correspond to the alloy AA6061. The first sample of each group (Q, S and U) was immersed in the Bonderite® Smutgo NCB bath. And the second one of each group (R, T and V) was immersed in the first acid etching bath.

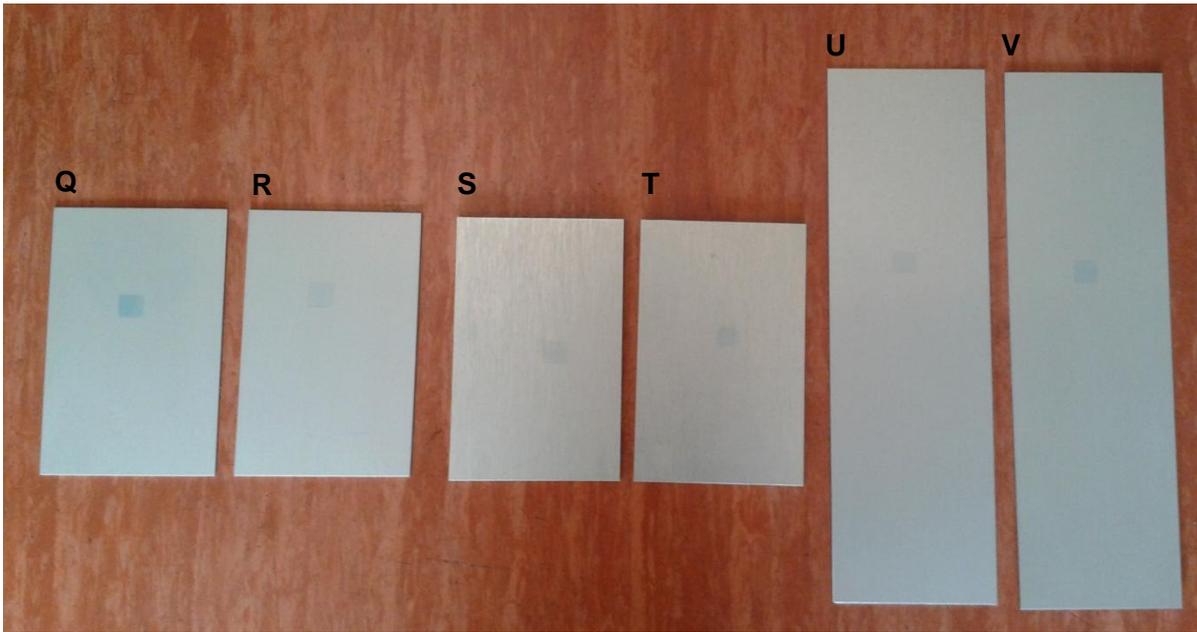


Figure 32. Potassium dichromate dye spot test: (Q) Alloy 2024 etching with Bonderite® Smutgo NCB, (R) Alloy 2024 etching with the first bath, (S) Alloy 7175 etching with Bonderite® Smutgo NCB, (T) Alloy 7175 etching with the first bath, (U) Alloy 6061 etching with Bonderite® Smutgo NCB and (V) Alloy 6061 etching with the first bath

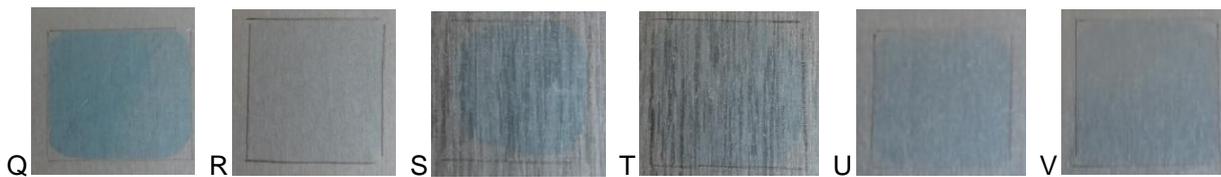


Figure 33. Potassium dichromate dye spot test expansion

As it can be seen, all the specimens have a colour intensity of 1. Although the first sample which corresponds to the alloy AA2024 and it was immersed in the Bonderite® Smutgo NCB bath, shows a slightly more intense colour, closer to intensity 2 than 1. The samples pass the test if its coloration is equal or less than intensity 2, therefore, from the results obtained it can be confirmed that all of them have successfully passed it.

It can be concluded that with the application of potassium dichromate on the TSA anodising film is achieved a good sealing for all the alloys, regardless of its chemical composition and its heat treatment.

The results of the test are very satisfactory on all the samples regardless the acid etching applied, since it is confirmed the loss of absorptive power on all of them. Therefore, in this case also it is proved that the Bonderite® Smutgo NCB can be a good non-chromate substitute for the first acid etching bath.

4.2.3. Paint adhesion

The adhesion test was performed on samples painted with primer and on samples painted with primer plus top coat. This test checks if the TSA coating film gives a good link between the aluminium alloy and the organic coating applied on the samples.

The procedures followed for the performance of the tests are explained in section 3.3.3. After its completion, the results obtained are evaluated comparing the detachment degree on the samples with the different possible degrees of detachment shown in Table 16.

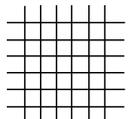
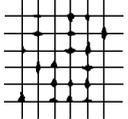
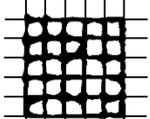
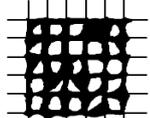
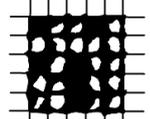
Classification	Description	Appearance of surface
0	The edges of the cuts are completely smooth; none of the squares of the lattice is detached	
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5% is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5%, but not greater than 15% is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15%, but not greater than 35% is affected.	
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35% but not greater than 65% is affected.	
5	Any degree of flaking that cannot even be classified by classification 4.	-

Table 16. Possible degrees of detachment

The classification shown above is valid for both, the dry and wet paint adhesion test. The results obtained are presented and discussed in the next sections.

4.2.3.1. Dry paint adhesion test

The dry paint adhesion test were performed on 9 samples painted with primer and 9 samples painted with primer plus top coat. In each of these two groups there are 3 specimens of each alloy tested (AA2024, AA7175 and AA6061). Apart from comparing the results obtained in the case of these different alloys and in order to compare the efficiency of the Bonderite® Smutgo NCB bath against the first acid etching bath, one sample of each these 3 was immersed in Bonderite® Smutgo NCB, in

particular the samples 1, 4, 7, 10, 13 and 16, and the rest of the specimens were immersed in the first etching bath.

The results obtained after the dry paint adhesion test are shown in the next Figures.

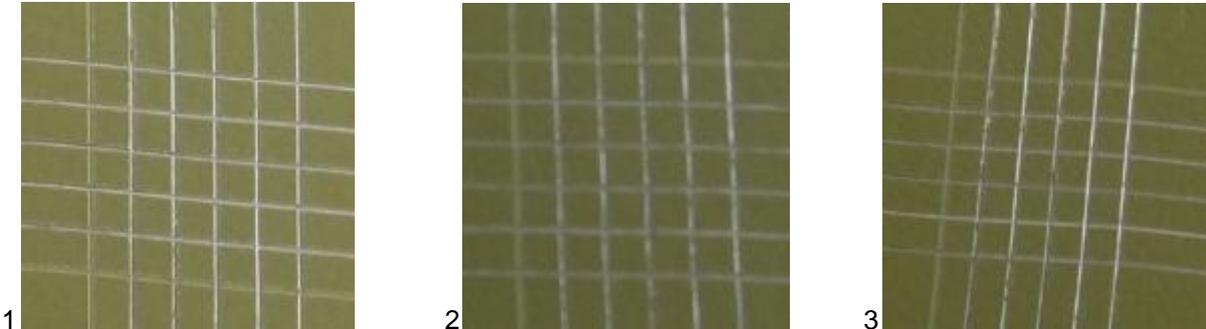


Figure 34. Alloy 2024 with primer after performing the dry paint adhesion test: (1) Bonderite® Smutgo NCB etching bath, (2,3) First etching bath

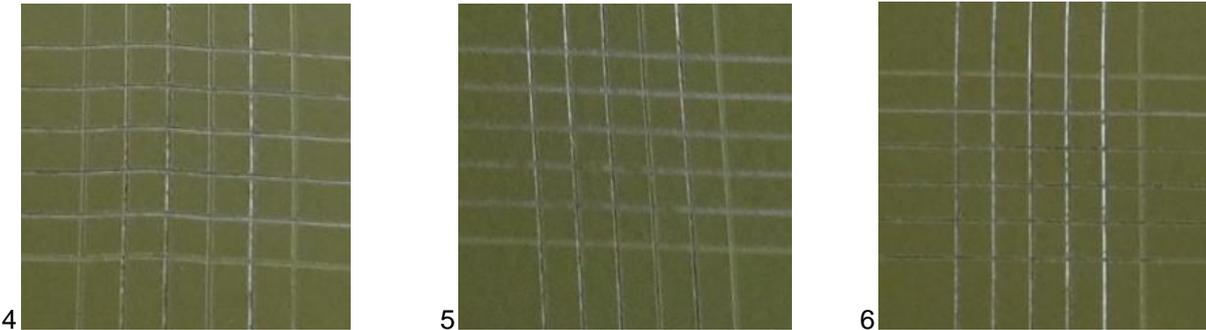


Figure 35. Alloy 7175 with primer after performing the dry paint adhesion test: (4) Bonderite® Smutgo NCB etching bath, (5,6) First etching bath

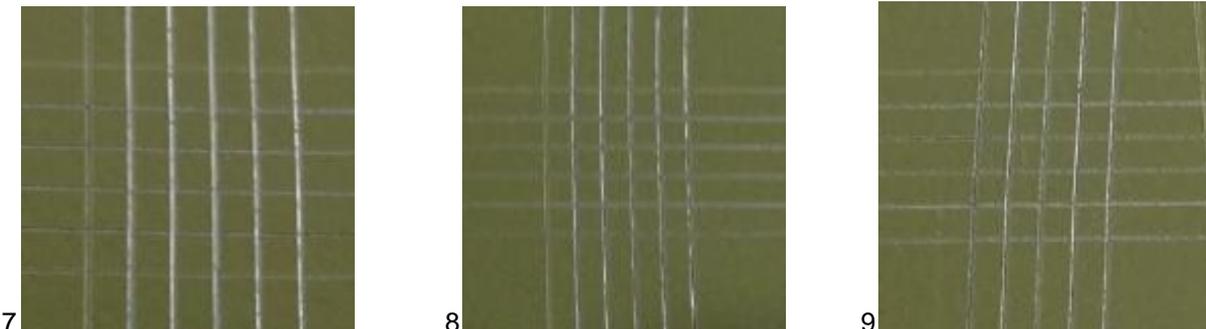


Figure 36. Alloy 6061 with primer after performing the dry paint adhesion test: (7) Bonderite® Smutgo NCB etching bath, (8,9) First etching bath

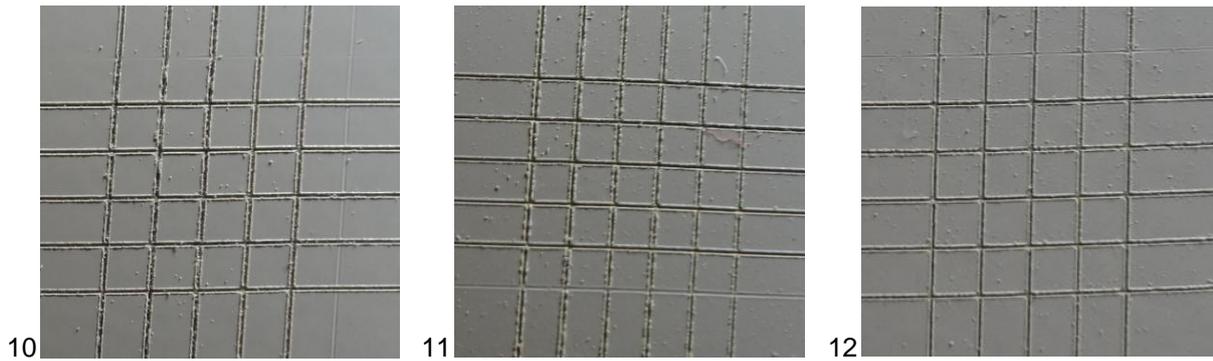


Figure 37. Alloy 2024 with primer plus top coat after performing the dry paint adhesion test: (10) Bonderite® Smutgo NCB etching bath, (11,12) First etching bath

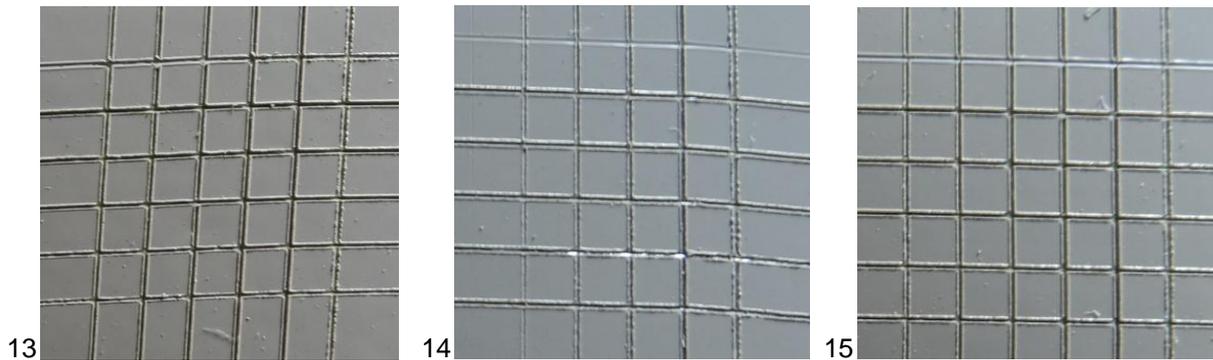


Figure 38. Alloy 7175 with primer plus top coat after performing the dry paint adhesion test: (13) Bonderite® Smutgo NCB etching bath, (14,15) First etching bath

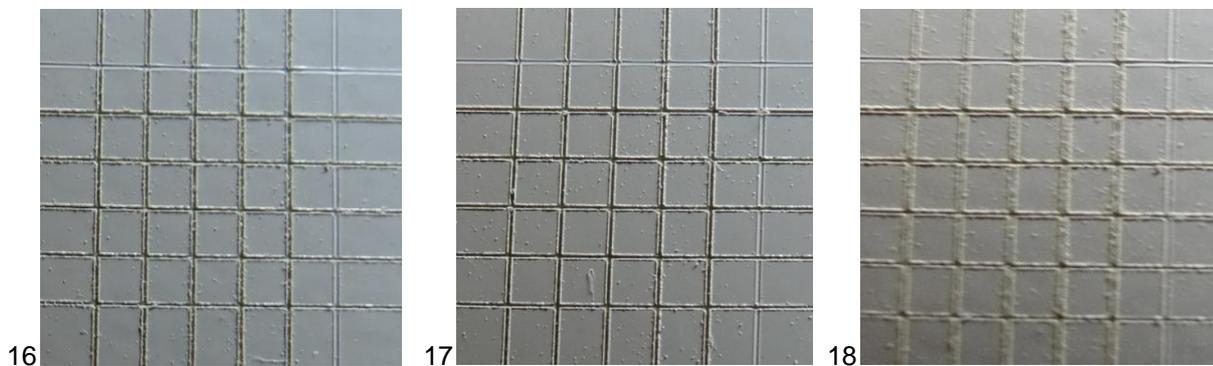


Figure 39. Alloy 6061 with primer plus top coat after performing the dry paint adhesion test: (16) Bonderite® Smutgo NCB etching bath, (17,18) First etching bath

Comparing the samples detachment degree after the performance of the test with the possible detachment degrees shown in Table 16, it can be seen that it corresponds to classification 0 on the samples painted with primer because none of the squares of the grid is removed.

In the case of the samples painted with primer plus top coat the same good results are achieved. There are not detachments of paint along the cuts or in their intersection, so it corresponds to classification 0, too.

So, it can be concluded that the TSA coating film gives very good adhesion between the three different alloys tested and the applied paint in both cases, with only primer and with primer plus top coat.

Analysing the differences between the samples immersed in the bath of Bonderite® Smutgo NCB with the samples which were submerged in the first etching bath, it can be seen that there are no significant differences as the degrees of paint detachment obtained in both cases are equal. This means that the Bonderite® Smutgo NCB, once again, could be a good non-chromate substitute for the etching bath.

4.2.3.2. Wet paint adhesion test

As in the previous case, the wet paint adhesion test was performed on 9 samples painted with primer and 9 samples painted with primer plus top coat. In each of these two groups there are three samples of the alloy AA2024, three of the alloy AA7175 and three of the alloy AA6061.

In the following Figures, it is shown the results obtained in the wet paint adhesion test.

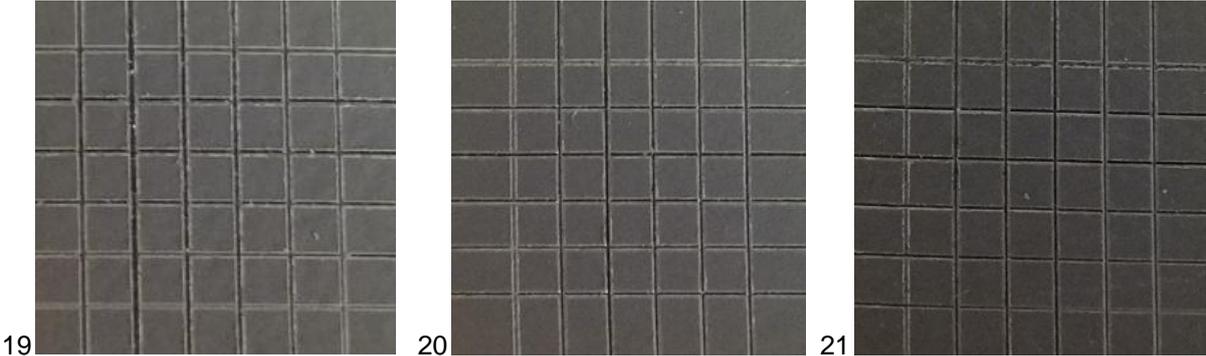


Figure 40. Alloy 2024 with primer after performing the wet paint adhesion test: (19) Bonderite® Smutgo NCB etching bath, (20,21) First etching bath

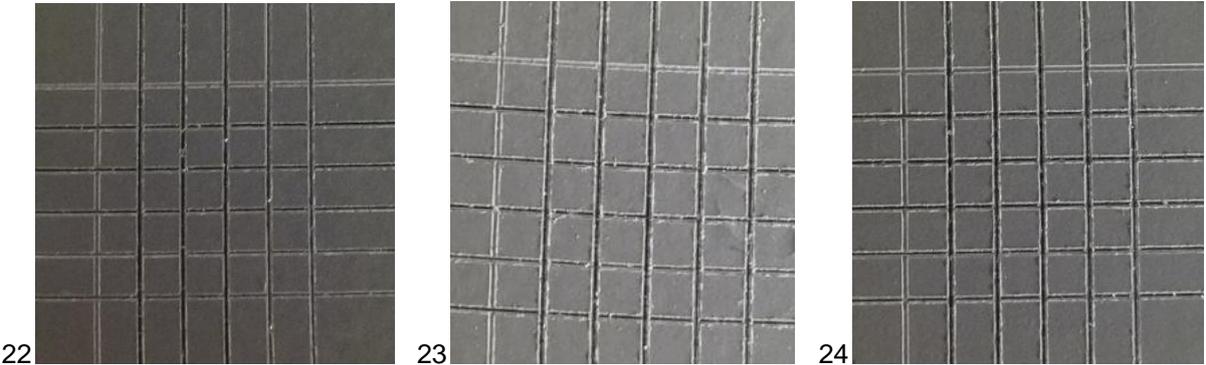


Figure 41. Alloy 7175 with primer after performing the wet paint adhesion test: (22) Bonderite® Smutgo NCB etching bath, (23,24) First etching bath

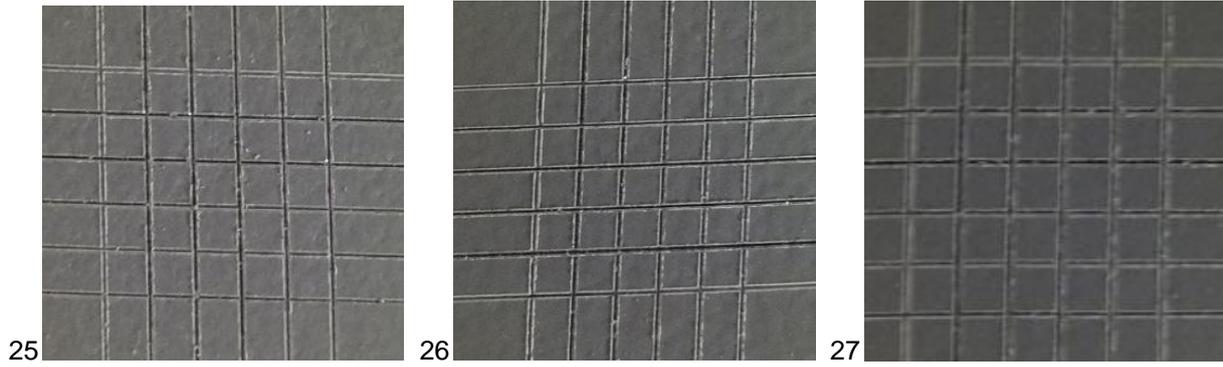


Figure 42. Alloy 6061 with primer after performing the wet paint adhesion test: (25) Bonderite® Smutgo NCB etching bath, (26,27) First etching bath

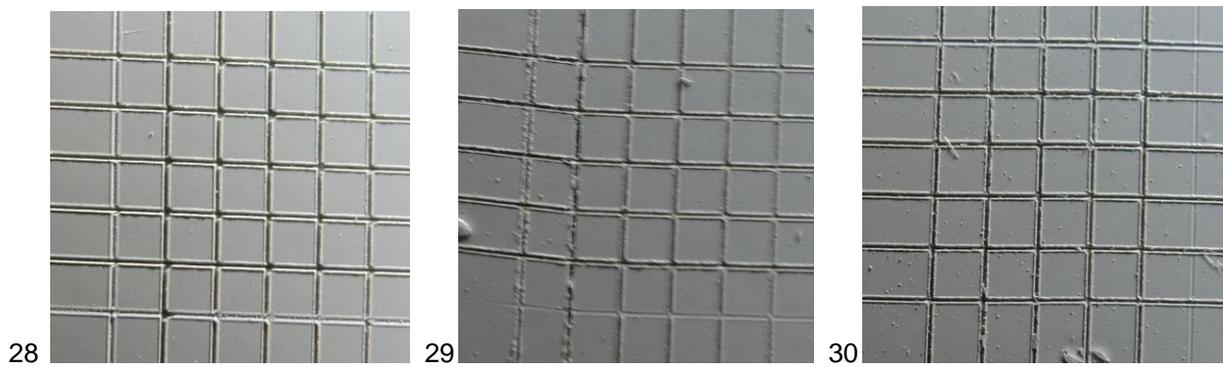


Figure 43. Alloy 2024 with primer plus top coat after performing the wet paint adhesion test: (28) Bonderite® Smutgo NCB etching bath, (29,30) First etching bath

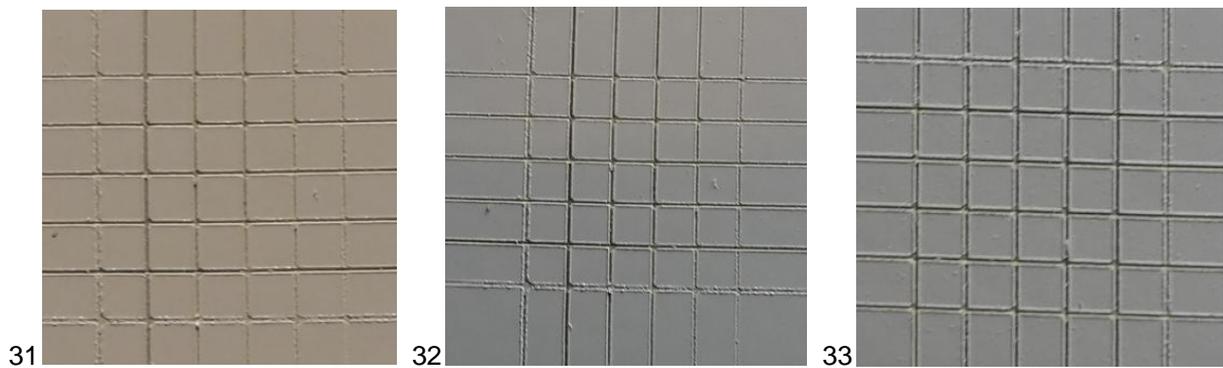


Figure 44. Alloy 7175 with primer plus top coat after performing the wet paint adhesion test: (31) Bonderite® Smutgo NCB etching bath, (32,33) First etching bath

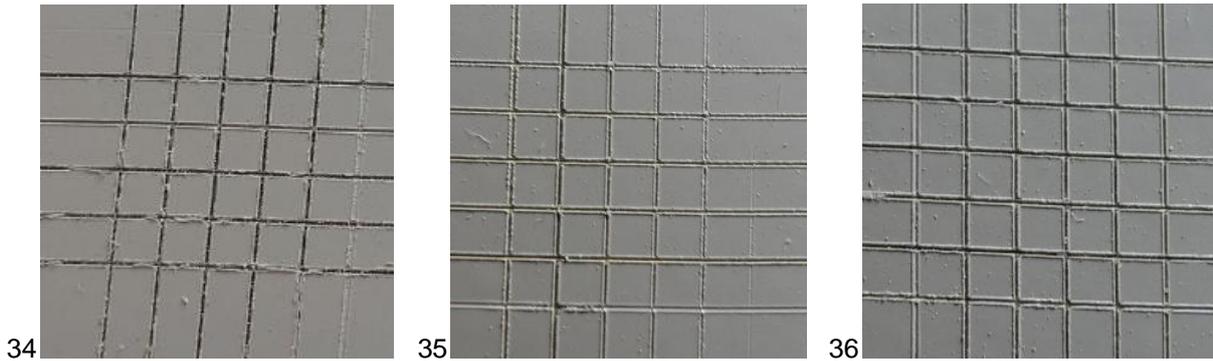


Figure 45. Alloy 6061 with primer plus top coat after performing the wet paint adhesion test: (34) Bonderite® Smutgo NCB etching bath, (35,36) First etching bath

Studying the results it can be seen that they are similar to those obtained in the case of the dry adhesion test. The samples painted with only primer do not show any paint detachment in the area where there is the grid, so they have a classification 0, regardless of the alloy and the acid etching bath.

In the case of the samples painted with primer plus top coat there are samples with small detachment flakes near where the grid lines cross each other. The detachment flakes can be seen in the three AA7175 specimens and on the sample 28 of AA2024. The classification that matches better for them is 1, because the paint detachment is only place near the intersection of the cuts not along them and the grid area affected is not greater than 5%. The rest of specimens can be classified as 0.

So, from the results obtained in the wet adhesion test this time also it can be concluded that the TSA film gives a good adhesion between the three alloys tested and the applied paint, in both cases, with only primer and with primer plus top coat. The same good results are achieved on the samples immersed in the first acid etching bath and on the specimens immersed in the Bonderite® Smutgo NCB bath. As it has not found significant differences, it is proved once again that this second bath is a possible and viable option without chromium for the acid etching.

5. Conclusions

After the performance of the quality tests, the main conclusions of this thesis can be summarized as follows:

- The TSA film obtained on the three alloys tested (AA2024, AA7175 and AA6061) is comparable to the CAA film in terms of thickness, coating weight, corrosion resistance and degree of sealing.
- The TSA anodic film provided good adhesion between the three aluminium alloys tested and the organic coating in use by Airbus, the primer 37035A and the topcoat Aerodur Finish C 21/100 UVR. Both of them passed with excellent results the dry and wet adhesion tests.
- Potassium dichromate post-treatment is compatible with the TSA anodic film on the three alloys tested. They provided the required corrosion resistance and achieved a high degree of sealing.
- The Chemical Conversion Coating Bonderite® M-CR 1200S Aero is compatible with the TSA anodic film on the alloys AA6061 and AA7175, however, not on the alloy AA2024. The first two passed with great results the salt spray test but on the AA2024 corrosion appeared after only 144 hours inside the salt spray chamber and it had a high grade of corrosion after 336 hours of exposure.
- Bonderite® Smutgo NCB did not affect the effectiveness of the TSA anodising and is completely compatible with the process. It is a good non-chromate substitute for the current etching bath composed of sodium dichromate, sulphuric acid and hydrofluoric acid.

6. Bibliography

- [1] Agency for Toxic Substances and Disease Registry (ATSDR), «Toxicological Fact Sheet for Chromium,» 2008.
- [2] EPA, US, "Integrated Risk Information Service (IRIS) assessment for hexavalent chromium," 1998.
- [3] European Chemicals Agency. Available: <http://echa.europa.eu/regulations/reach>. [Accessed April 2015].
- [4] REACH, Annex XIV to Regulation (EC) No 1907/2006, 2013.
- [5] F. Museux y R. Theilmann, «Introducing more eco-efficient chemical treatments for aircraft structure,» *FAST 45 Airbus Technical magazine*, p. 35, December 2009.
- [6] OGMA ONS-000097, *Oxidação anódica crômica do alumínio e suas ligas*.
- [7] Airbus AIPI 02-01-001, *Chromic acid anodizing of aluminium alloys*.
- [8] Boeing, "Method for anodizing aluminium". United States Patent US 4894127, 16 January 1990.
- [9] Airbus, "Airbus," 2015. Available: <http://www.airbus.com/>. [Accessed April 2015].
- [10] C. Ferrer Giménez y V. Amigó Borrás, *Tecnología de materiales*, Universidad Politécnica de Valencia, 2003.
- [11] Group Cleaning Technologies, "Ultrasonic cleaning: Fundamental Theory and Application," 2009. Available: <http://www.ctgclean.com>. [Accessed May 2015].
- [12] Airbus AIPI 02-01-003 Issue 1, *Tartaric sulphuric anodising of aluminium alloys for corrosion protection and paint pre-treatment*.
- [13] European Space Agency, *Assessment of Chemical Conversion Coatings for the Protection of Aluminium Alloys*, ESA Communication Production Office, 2008.
- [14] ASM, "ASM Aerospace Specification Metals Inc.," Available: <http://asm.matweb.com>. [Accessed March 2015].
- [15] M. G. Rubio, *Optimisation of a non-chromium-containing tartaric acid/sulphuric acid anodising bath for aluminium alloys for aerospace industry application*, 2009.
- [16] ASTM B244, *Standard Test Method for Measurement of thickness of anodic coatings on aluminium and of other nonconductive coatings on nonmagnetic basis metals with eddy-current instruments*.
- [17] MIL-A-8625, *Anodic coatings for aluminium and aluminium alloys*.
- [18] ASTM-B-117, *Standard Practice for Operating Salt Spray (Fog) Apparatus*.
- [19] ISO 2409, *Paints and varnishes – cross-cut test*.
- [20] EN 3665:1997, *Aerospace series – Test methods for paints and varnishes – Filiform corrosion resistance test on aluminium alloys*.

- [21] ISO 9227, *Corrosion test in artificial atmospheres – Salt spray tests.*
- [22] ISO 2360:2005, *Non-conductive coatings on non-magnetic electrically conductive basis materials – Measurement of coating thickness – Amplitude-sensitive eddy-current method.*
- [23] AITM3-0030, *Titration of sulphuric and tartaric acid anodizing electrolytes.*
- [24] ISO 2143:2010, *Anodizing of aluminium and its alloys – Estimation of loss of absorptive power of anodic oxidation coatings after sealing – Dye spot test with prior acid treatment.*
- [25] C. Vargel, *Corrosion of aluminium*, Elsevier Ltd, 2004.
- [26] G. Boisier, N. Pébère, C. Druetz, M. Villatte y S. Suel, *FESEM and EIS Study of Sealed AA2024 T3 Anodized in Sulfuric Acid Electrolytes: Influence of Tartaric Acid*, 2008.
- [27] P. Ocon, M. Garcia, I. Garcia y M. A. Lavia, «Procedure for anodising aluminium or aluminium alloys». United States Patente US 2009/0107848 A1, 30 April 2009.
- [28] Alenia, "Anodizing process with low environmental impact for a woodpiece of aluminium or aluminium alloys". United States Patent US 2002/0157961 A1, 31 October 2002.
- [29] Boeing, "Fungus resistant boric acid-sulfuric acid anodising". United States Patent US 6149795, 21 November 2000.
- [30] Airbus, "Procedure for anodising aluminium or aluminium alloys". Spain Patent EP 2 055 810 A2, 06 May 2009.
- [31] Airbus, «Procedure for anodising aluminium or aluminium alloys». Spain 23 January 2013.
- [32] Embraer NE 40-030, *Aluminium and its alloys – Anodic coatings in chromic acid.*
- [33] Westland WHPS 077, *Anodic oxidation of aluminium and aluminium alloys in chromic acid.*
- [34] EADS-CASA I+D-P-416, *Anodizado Tartárico-Sulfúrico del aluminio y sus aleaciones.*
- [35] Agusta STA 100-80-01, *Chromic acid anodising.*
- [36] Airbus AITM7-0009, *Detection of fungal contamination in TSA anodisation baths – Vitality test.*
- [37] Airbus AITM7-0008, *Microbiological monitoring of TSA anodisation baths – Bait substrates.*
- [38] Dassault DQQT 0.8.3.0002, *Oxydation Anodique Chromique.*
- [39] EADS-CASA I+D-P-060, *Pintura (especificación general).*
- [40] EADS-CASA I+D-P-064, *Pintura de piezas elementales y conjuntos metálicos.*
- [41] Airbus AIPS 02-01-003 Issue 1, *Tartaric sulphuric anodising of aluminium alloys for corrosion protection and paint pre-treatment.*