Surface treatments for aluminium alloys

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Abstract. Typically, in contact with the atmosphere, the aluminium surface is covered with an aluminium oxide layer, with a thickness of less than 1-2μm. Due to its low thickness, high porosity and low mechanical strength, this layer does not protect the metal from corrosion. Anodizing for protective and decorative purposes is the most common method of superficial oxidation processes and is carried out through anodic oxidation. The oxide films, resulted from anodizing, are porous, have a thickness of 20-50μm, and are heat-resistant, stable to water vapour and other corrosion agents. Hard anodizing complies with the same obtains principles as well as decorative and protective anodization. The difference is in that hard anodizing is achieved at low temperatures and high intensity of electric current.

In the paper are presented the results of decorative and hard anodization for specimens made from several aluminium alloys in terms of the appearance of the specimens and of the thickness of the anodized.

1. Introduction

Some metals and alloys are protected against corrosion by coating with inorganic layers (films) made by chemical and electrochemical processes. In the industry are frequently applied films of oxides, phosphates and chromates.

Oxide and chromate films are used for decorative finishing of parts, carcasses of measuring and control devices. By coating with oxides and phosphates, are improved some properties of metal surfaces such as hardness, wear resistance, electro-insulating properties, etc.

Aluminium and its alloys are one of the most important categories of materials used by modern technology due to the advantages of low specific gravity, high thermal and electrical conductivity, good corrosion resistance, good mechanical features, easy machining, etc. Today, Aluminium -based alloys are the world's second metallurgical product, after steel, although the knowledge history of this metal is shorter than two centuries [1]. In the form of pure metal, aluminium is less used, but in the alloyed state it is the most used non-ferrous metal.

The aluminium trioxide film, which is formed, even at ambient temperature, is compact, waterproof and strongly adherent to metal. This makes aluminium good corrosion resistance, even in aggressive environments such as organic acids, seawater, humid atmospheres, etc. Aluminium is slightly attacked by nitric acid and sulfuric acid, instead hydrogen chloride and bases easily dissolve it. The presence of certain impurities significantly reduces the resistance of aluminium to corrosion [2].

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In order to be easily recognized, Aluminium Association and the American National Standard Institute has proposed a system of symbolization of aluminium alloys that has been rapidly assimilated by all aluminium producing countries [3].

Figure 1. General classification of aluminium alloys

Another classification of aluminium alloys was also made according to the main alloying element by associating them in eight main series, each series containing a four-digit number [3], [4].

2. Surface treatment of aluminium alloys

Inorganic layers are used for the protection of metals subjected to atmospheric corrosion. Oxidation and phosphating are performed to obtain intermediate layers before applying paint layers.

Oxide and chromate films are used for decorative finishing of parts, carcasses of measuring and control devices. By coating with oxides and phosphates [5], are improved some qualities of metallic surfaces such as hardness, wear resistance, electro-insulating properties, etc.

Of the most common surface treatment processes for aluminium are anodizing, hard anodizing, chromating and bright dip (chemical polishing).

2.1. Anodizing

The process of obtaining oxide films on the surface of aluminium parts or its alloys by anodic oxidation is called anodization. Anodizing for protective and decorative purposes is the most common of superficial oxidation processes [6].

The films of oxide formed by anodization, are porous, have a thickness 20-50 microns, are heat resistant, stable to the action of water vapour and other corrosive agents. The biggest disadvantage of these films are limited elasticity and high hygroscopicity [7].

The aluminium oxide film qualities are improved by introducing the anodized pieces into the 90°C water. This process is called sealing the pores. The sealing of the pores is determined by the hydration of aluminium oxide, with the formation of crystals of type Al₂O₃·nH₂O, that having low specific weight and high volume, sealing the pores from this layer.

Oxide films can be impregnated with various substances, such as paraffin, insulation paints and some polymers. Impregnation reduces the hygroscopicity of the film and increases corrosion resistance [8]. Aluminium oxide is very porous, has a high absorption capacity of organic and inorganic dyes and anti-corrosion paints, thus achieving decorative effects on the surface of the pieces [9].

Colour anodized aluminium is achieved by deposition of coloured particles in the pores of the anodized layer (electrolytic staining) after the anodization phase and before the sealing phase.
Most often, as an electrolyte is used a solution of 10-20% H₂SO₄ at 15-30°C. It works at a voltage of 12-15V achieving variable current densities, from a few A/dm² at first, up to several hundred A/dm² at the end [10].

Sulfuric acid, strongly electrolyte, dissociates according to the equation:
\[ \text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \]  \hspace{1cm} (1)

Reactions that occur at the electrodes of an electrolytic cell are:
- to cathode: \[ 2\text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \uparrow \]  \hspace{1cm} (2)
- to anode:
  \[ 2\text{OH}^- - 2 \text{e}^- \rightarrow \text{H}_2\text{O} + \text{O} \]  \hspace{1cm} (3)
  \[ \text{SO}_4^{2-} - 2 \text{e}^- \rightarrow \text{SO}_3 + \text{O} \]
  \[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]
  \[ 2\text{Al} + 3\text{O} \rightarrow \text{Al}_2\text{O}_3 \]

If it is desired to obtain thick oxide films with special properties, the purity of the aluminium subjected to oxidation must be very high.

2.2. Hard anodizing

Hard anodizing follows the same training principles as decorative and protective anodizing. The difference consists in the fact that hard anodizing is done at low temperatures and high currents. The pores of the hard anodized layer are smaller than the classic anodizing.

In this case, the anodized layer is very hard, abrasion-resistant but still remain porous. Due to this very hard layer of aluminium oxide, the hard anodized parts are suitable for wide range of applications, from military applications to multitude of other applications such as parts for the electrical industry, mechanical parts, aluminium cookware, etc [11].

Hard anodization is made in a sulfuric acid bath containing 180-200g/l of acid and a small amount of dissolved aluminium. The operating temperature is controlled between -5...0°C, but in some cases an acceptable oxide layer can be obtained at slightly higher temperatures.
The resulting porous oxide may then be coloured and sealed, but the final colour limitations are determined by the type of oxide and the used colour.

2.3. Chromating
Chromating is not an aluminium-specific treatment, chromating is specific to steel parts, where chromium-alloyed steels have good wear resistance, corrosion, and high temperature resistance [12]. Chromating can be applied not only to aluminium alloys but also to zinc, cadmium, copper, silver, magnesium and tin alloys.

For decades, hexavalent chromium treatment has been standard for aluminium. More recently, superficial treatments with these chromium-based products are subject to environmental, health and safety pressures.

Currently, the product used for chromating is SURTEC 650 (Tri-Crom aluminium passivation product - Best Available Technology for Aluminium Pre-treatment) [13]. The metallic surface of the aluminium piece turns into a stable barrier, mostly oxide layer. This layer prevents or slows down the corrosive attack, resistance to electric contact is small, improve the adhesion of the coatings, such as paints, sealing materials or some types of glues.

Chromating with SURTEC 650 is a passivation procedure for the surface of aluminium parts that ensure an excellent corrosion resistance up to 100°C. After treatment with SURTEC 650 the surface of the parts can be painted in electrostatic field, the chromium layer ensuring a very good adhesion of the paint.

2.4. Chemical polishing (Bright Dip)
Bright Dip is a chemical polishing process for the piece, and can be considered a preparatory operation for anodizing consisting in a chemical attack on the aluminium parts using a mixture of acids. The effect is partial and preferential dissolution of surface pieces resulting in a mirror surface of this. The method replaces electro-polishing or electroplating procedures for specialized articles such as car ornaments, picture frames, cosmetic containers and much more [14].

Problems related to aluminium cleaning are not simple, due to a sensitivity of the metal and its reactivity with many commonly used cleaning solutions. Are used an alkaline solutions, detergents or acidic cleaners, separately or together in various combinations.

Alkaline solutions are used to eliminate the drawings and traces of oils and glue. Even slightly alkaline cleaning solutions will attack Aluminium, especially at higher temperatures unless is used an inhibitor. An ideal cleaning cycle should include the acid cleaning as last operation.

Among the types of acids used for cleaning are:
- phosphoric acid, which leaves a clean surface without oxides and with a special quality of the surfaces of the piece;
- sulfuric acid, which requires corrosion inhibitors, without the parts would be strongly attacked;
- citric acid, which does not have great cleaning power, leaves the surface activated for the next processing steps. They are used where there are restrictions on the use of phosphoric and sulfuric acids.

After cleaning, the surface is activated is formed only from the base metal, it is not covered by any oxide and is prepared for the following operations.

3. Experiments made with aluminium alloys

Experimental tests were performed in SC ANOROM SRL consisting in colourless and black anodization versions with and without satin finish and hard anodization.

A quick review of the behaviour of the various alloys on anodization [15] is presented below:

- 1000 alloy series (pure aluminium). They respond well to anodizing treatment. The anodized layer is the more transparent as the aluminium is pure;
- 2000 alloy series (copper alloys). The copper from this alloy dissolves during the treatment, resulting after anodization an unaesthetic area (milky) [16]. The colouring of this alloy is also bad due to copper that prevents the aluminium oxide layer being uniformly deposited, that also leads to the decreasing of surface hardness and abrasion resistance;
- 3000 series alloys (manganese alloys). At concentrations above 1% Mn the anodized layer is bluish grey;
- 5000 alloys series (magnesium alloys). It performs well with anodizing. Up to a concentration of 3% Mg the anodized layer is colourless. If the magnesium concentration is greater than 3%, the anodized layer becomes grey. Sometimes a slight yellowish tendency can be observed if the alloy contains traces of manganese or chrome;
- 6000 alloys series (magnesium and silicon alloys) behave very well at anodizing and colouring, with very homogeneous anodized layer. To pieces made from this alloy can be applied satin finish to obtain a matte appearance of the surface. At thicknesses of the anodized layer over 30μm, the surface of the parts becomes dark grey;
- 7000 alloy series (zinc alloys), as the anodized layer thickness is greater as can be seen better surface appearance of the greenish yellow anodized parts. Some alloys of the 7000 series may also contain copper (eg 7075 alloy) and behave at anodization as a 2000 alloy series, the anodized surface being unaesthetic.

The samples were provided by COLOR METAL SRL through SC ANOROM SRL. These consist of specimens taken from different extruded bars from 2017 SK03, 5083 SA 02, 5083 SG 0, 6082 SF02, 7021 and 7075 aluminium alloy grade.

![Figure 5](image_url)

**Figure 5.** Examples of aluminium specimens, 5083 and 6082 grade

In Figure 5 shows a few specimens provided by this company. As can be seen from the Figure, the specimens are protected with a plastic foil against oxidation, a film that is removed before fitting into the mounting brackets.
In order to perform the anodization, the specimens will be fixed in special supports. They are made from titanium and will not oxidize when the pieces are treated. The fixing mode and construction of this support is shown in Figure 6.

![Figure 6. The fastening mode and construction of fixing support](image)

To avoid possible defects, the electrical contact between the piece and the support should be as good as possible, in other words, the piece should be tightened as much as possible. Figure 7 shows the pieces fixed to the support before being treated.

![Figure 7. Test specimens ready for anodizing operation](image)

In order to observe the difference generated by different chemical composition (for each grade of aluminium alloy), all parts have been treated respecting the same parameters, namely alkaline degreasing, satin finishing, anodization, rinsing water, pore sealing.

All operations, parameters and technologically time are tracked and passed into a manufacturing order [10].

The supports with test specimens are handled by automatic cranes that can operate both automated and manual with operator.

It is very important to rinse the pieces when passing from one bath to another. Pieces was rinsing repeatedly until when removing from the rinse bath on the surface of the piece we have a continuous film of water.

For colourless satin pieces a technological flow involves the following steps: alkaline degreasing; current rinse; satin finishing operation; static and current rinse; introducing the test specimens into the nitric acid bath; current rinse; anodic oxidation; static and current rinse; sealing pores; current rinse – presented in Figures 8-10.
Figure 8. Alkaline degreasing

Figure 9. Satin finishing (left) and black colouring (right) of test specimens

Figure 10. Anodizing (left) and current rinse (right)
In the case of non-satin or black anodizing process, test specimens are treated with additional steps corresponding to the technological operation added or, if necessary, removed. The following Figures show aspects of the anodizing operation with satin finishing.

In the case of hard anodization the experiments was made in another periods of time, this installation is not used every day. Through this process was obtained a special values of surface hardness, which according to the literature is usually between 600...800HV. In this case the thickness of the superficial layer is very small, and hardness cannot be measured by the usual methods.

The thickness of the anodized layer is measured with a portable Foucault current device for thin layer [10]. In Figure 11 is presented a comparison between the thickness of the natural layer of aluminium oxide and the thickness of the aluminium oxide layer after anodizing.

![Image](image_url)

**Figure 11.** Comparison between the thickness of the natural layer of aluminium oxide and the thickness of oxide layer after anodizing

### 4. Results and discussions

After the experiments carried out on all 6 categories of materials, were obtained the following layer thicknesses, and shown in the Table 1.

| No | Material    | Colourless anodizing thickness of oxide layer, µm | Colourless anodizing thickness of oxide layer, µm | Black anodizing + Satin finishing thickness of oxide layer, µm | Black anodizing thickness of oxide layer, µm |
|----|-------------|--------------------------------------------------|--------------------------------------------------|---------------------------------------------------------------|---------------------------------------------|
| 1. | 2017 SK03   | 8,64                                             | 8,44                                             | 13,26                                                         | 10,80                                        |
| 2. | 5083 SA 02  | 36,30                                            | 32,05                                            | 38,25                                                         | 33,75                                        |
| 3. | 5083 SG 0   | 39,20                                            | 37,30                                            | 45,36                                                         | 43,35                                        |
| 4. | 6082 SF02   | 22,36                                            | 20,24                                            | 21,10                                                         | 20,58                                        |
| 5. | 7021        | 43,20                                            | 33,30                                            | 45,90                                                         | 36,25                                        |
| 6. | 7075        | 32,75                                            | 33,60                                            | 36,70                                                         | 38,45                                        |

From the data shows Table 1 results that the 2017 SK03 aluminium alloy had the worst behaviour in all anodizing variants, and the 5083 SG 0 and 7021 aluminium alloys had the best behaviour for almost all anodizing variants.

For a better analysis of the data resulting from these experiments, will be presented in the Figure 12 the same results, but in the graphical form.
In Figure 13 show the colour variations for the vast majority of anodized parts in all anodizing variants.

It is interesting to look at the influence of alloying elements on the behaviour of different aluminium alloys in the different anodizing variants. Thus, depending on the average alloying element content, it is possible to represent a graphically variation of the thickness of the anodized layer for the studied alloys.

The previous graphical dependencies were made for the colourless anodizing variant with satin finishing, and in term of the chemical composition, were worked with the average values imposed by the standard.

In graphical dependence of the thickness of the anodized layer, depending on the average content of copper required by the standard, there is a tendency to decrease the thickness of the anodized layer with the increase of the copper content in the alloy for both variants.

**Figure 12.** Layer thicknesses obtained from different anodizing variants

**Figure 13.** Comparison between colour palette obtained at colourless anodizing (left), colourless anodizing + satin finishing (center) and hard anodizing (right), for all aluminium grade
In the case of the graphical dependence of the thickness of the anodized layer, depending on the average content of magnesium required by the standard, it observes a maximum thickness of the anodized layer thickness for 1.3...1.7% Mg. A further increase in magnesium content has adverse effects on the thickness of the anodized layer. This dependences is presented in Figure 15.

Such graphical dependencies can be made for all anodizing variants and all alloying elements present in the chemical composition of the aluminium alloy.

The thickness of the anodized layer depends also on the holding time in the anodizing bath, in other words, simple or multiple dependencies can be identified depending on the holding time in the anodizing bath and the chemical composition of the anodized material.
5. Conclusions
Several conclusions can be drawn from the experiments as follows:
- the defects resulting from the production process tend to zero, they can occur mainly due to the improper fixing of the parts that will be anodized in the fixing supports;
- another possible cause of the parts with defects may be a piece made from an material different from that of the entire product group. SC ANOROM SA does not control the chemical composition of the parts just treats them superficially;
- from the data on the Table 1 we can see that the 2017 SK03 aluminium alloy has the worst behaviour in all anodizing variants, and the 5083 SG 0 and 7021 alloys has the best behaviour for almost all anodizing variants;
- the thickness of the anodized layer depends on the maintaining time in the anodizing bath;
- colour of the alloy in the case of colourless anodization with satin finish and without satin finish depends also on the maintain time in the anodizing bath;
- I think it would be of great importance to measure the hardness of the anodized layer, in which case can be made simple or multiple correlations to determine optimal areas for hardness;
- the process and stages of anodization are very well optimized, the defect rate is almost zero.

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