

THE INFLUENCE OF SULFURIC ACID ANODIZING ELECTROCHEMICAL PROCESS ON SURFACE TREATMENT ADHESION

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ABSTRACT: This paper presents the influence of sulphuric acid anodizing electrochemical process on surface treatment adhesion, by testing two distinct scenarios. The paper presents the general context in the aerospace industry related to product service life, as well as give in depth information related to the sulphuric acid anodizing electrochemical process. It presents the general principle of sulphuric acid anodizing, equipment used and the results of the process. Details are provided related to surface treatment, paint application techniques, also explanation of adhesion testing technique used to collect the result for this paper. Conclusions are drawn based on the tests performed, which clearly show evidence of the influence of sulphuric acid anodizing process on surface treatment adhesion.

KEYWORDS: sulphuric acid anodizing, surface treatment, adhesion, electrochemical process, oxide layer, aerospace.

1. INTRODUCTION

In the aerospace industry, the maintenance of the aircraft represents the biggest contributor to aircraft inoperability intervals. These intervals are determined, by the type of maintenance activity, performed on the aircraft, such as:

- Planned
 - Type A check, with a duration of approximately 60 hours;
 - Type B check, with a duration of approximately 170 hours;
 - Type C check, with a duration of approximately 1-2 weeks;
 - Type D check, with a duration of approximately 2 months.
- Unplanned
 - In the case of problems identified on the aircraft (functional problems, incidents during takeoff or landing, in flight incidents, etc.) [1].

The reduction of these times of inoperability, of the aircraft, is very important for any airline company, who wishes to use the aircraft to its fullest potential. These requirements related to maintenance times, are flowed to the aircraft producers, which get the request for a product, which is easy to maintain and with the longest life cycle possible.

By analysing, the aircraft structure, which consists in a large proportion of metallic materials, the rest being composite materials and other materials. The use of metallic materials in the structure of the

aircraft makes it susceptible to corrosion, in some areas, where these materials are used and where the protection applied to the metallic materials is not resistant enough.

The identification of methods to protect the metallic materials, especially aluminium, which are more efficient from resistance to wear point of view, are key to the reduction of the maintenance times during the aircraft life cycle.

One of the key characteristics of a surface treatment system, which allows a better resistance to wear, is the adhesion of the surface treatment system to the base material. Without this adhesion or with a reduced adhesion, the components of the aircraft structure are susceptible at any moment, especially in passenger areas, to corrosion, caused by the deterioration of the surface treatment system due to hits or repeated friction.

One of the methods that increase surface treatment adhesion is the application of an electrochemical process, called sulphuric acid anodizing, on the base material, in order to prepare the material for surface treatment application [2].

2. SULPHURIC ACID ANODIZING

2.1 Principle

Anodizing is the process that consists in the immersion of a component, in an acidic substance (in this case sulphuric acid) and application of a continuous current, in order to create a homogeneous and resistant layer of oxide at the surface of the component [3].

As its name suggests, during anodizing, the components are fixed in an electric circuit and are powered with positive charge, fulfilling the role of an anode. The negative charge is transmitted to a component of the equipment, which is positioned on the edge of the tank and is distributed evenly on the sides of the work area, called cathode.

In order for the anodizing process to provide the desired effect, it is necessary to maintain a set of electrical and chemical parameters, as well as the temperature, between some limits:

- Direct electrical voltage, between 12 and 18 V;
- Direct current, as a function of the number of components;
- Sulphuric acid concentration, between 180 and 220 g/L;
- Temperature of the acidic substance, between 16 and 20 °C;
- Component immersion time in the tank, based on the thickness requirement.

2.2 Process

The process of creating the homogenous and resistant oxide layer starts with a careful preparation of the base material.

In the case that in some areas of the component, anodizing is not required; that area needs to be masked with an adherent and resistant material, prior to cleaning and anodizing process. The material used in the masking process needs to be cut to size to desired dimension, prior to application.

Next step is to clamp the components requiring processing on the anodizing support, which allows the connection to the positive charge of the rectifier. The clamping on the anodizing support needs to be done with enough fixing points, in order to allow the application of high currents, without damaging the components to be processed, in the fixing area. At the same time the position of the components needs to offer enough inclination, in order to allow the elimination of potential gases trapped during component immersion in tank and of the acidic substance during component extraction from tank.

The force applied to the clamping elements needs to be sufficient to secure the components during handling operation, but not too high to cause component deterioration.

Once correctly fixed, the components are processed for pre-cleaning, which has the role of preparing the surfaces to be anodized, such that any contaminants from the surface of the component are removed, in

order not to influence negatively the anodizing electrochemical process.

The first pre-treatment tank is the alkaline degrease, where the components are immersed in order to remove contaminants such as emulsions, oils, fingerprints, ink traces, stains, etc.

The alkaline degreasing step is followed by an alkaline pickling step, which allows the removal of a metal and oxide layer, in order to obtain a fine texture, by levelling the imperfections of the surface of the treated components. Following this process all contaminants existent on the surface of the components before the pre-treatment process, are completely removed. If this is not done, the anodizing process is negatively impacted, as well as the subsequent processes.

After alkaline pickling, a black layer specific to this step can be seen at the surface of the treated components, it is removed by acid pickling. Together with this layer, it is removed also a negligible layer of material, which prepares the surface in terms of reducing the electrical resistance.

A last step in the pre-treatment process is the rinsing process, which is designed to eliminate the potential chemical substances remaining on the surface of the components to be anodized.

Once the treated components are pre-cleaned, the electrochemical anodization process with sulphuric acid can start, by completely immersing the components in the sulphuric acid tank and coupling the anode support to the electrical circuit.

After powering the circuit with a high direct current and low direct voltage, hydrogen is released at the surface of the cathode and oxygen is released at the surface of the treated components (anode), which contribute to the creation of a layer of oxide at the surface of the components.

This oxide layer is the key characteristic of the treated product, providing a protection superior natural oxide, but also due to the oxide layer morphology that has a high enough porosity to create the ideal material surface for the adhesion of the following layers of surface treatment.

The thickness of the aluminium oxide layer created on the surface of the treated components after the anodizing process is determined by the parameters listed in the Principle chapter, the most important being the immersion time, which can be easily controlled with the anodizing equipment.

As with the pre-cleaning process, the anodizing process is followed by a rinse step, which is

intended to remove any residual chemical substances left over at the surface of the treated components.

The anodizing process is completed by drying the treated components or, if desired, the oxide layer can be sealed by immersion in a hot water tank. This type of protection is an anticorrosive form of protection, however, the wear resistance is low and the adhesion of the paint is impaired.

During the inspection after the anodizing process, following criteria are checked:

- Thickness of oxide layer,
- The weight of the oxide layer (on specimen),
- Corrosion resistance of the oxide layer (on specimen),
- Continuity of the oxide layer,
- General appearance check (scratches, corrosion, etc.)
- Removal of contaminants check (fats, oils, ink, etc.)
- The overall appearance of the oxide layer (continuous, smooth, etc.)
- Assessment of the clamping areas for burn marks.

2.3 Equipment

Anodizing with sulphuric acid can be achieved via a manual process by using tanks and the immersion is performed manually. In this case, the result of the anodizing process relies heavily on the human factor, having a poor repeatability of the results, compared to the automated version.

For a net superior repeatability, most manufacturers use the automated option, by using an automatic anodizing line, which allows a very good control over the process parameters.

The automatic anodizing line is an assembly of the following equipment:

- Succession of chemicals-resistant tanks, dimensioned on the basis of product requirements (product size);
- Heaters, for the tanks where the temperature needs to be maintained;
- Recirculation and agitation systems, in order to maintain solution uniformity;
- Level, pH, conductivity sensors, etc.;
- Rectifier, to convert alternating current to direct current;
- Electrical power circuit, which allows the supply of the direct current to be used for the anodizing process;
- Command and control panel, which allows the operator of the anodizing line continuous monitoring

of process parameters and possible unplanned events;

- Slide bridge, which is controlled by the control panel and performs the immersion of components in tanks;
- Beam and anode support, which allow the component to be fixed, manipulated and powered at the time of anodizing process.

2.4 Result

Following the anodizing process, the result observed on the aluminium components, in the case of this paper, is a homogeneous and resistant aluminium oxide coating.

The anodic layer immediately after the anodizing treatment has, among other things, a high porosity and a thickness of the layer, which is generally between 10-15 microns.

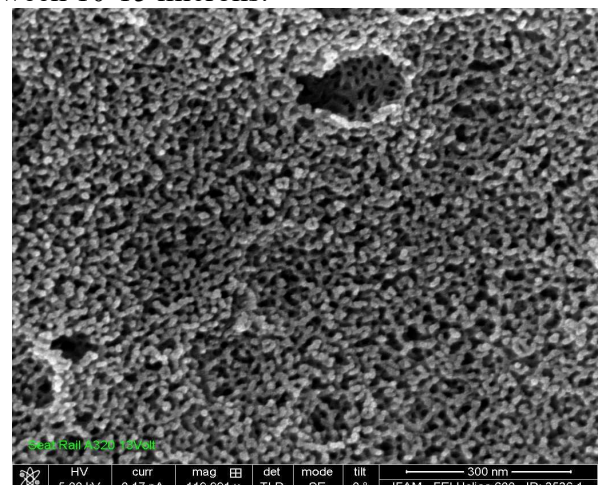


Figure 1. Anodic layer morphology with scanning electron microscope

This porosity can be observed with a scanning electron microscope (Figure 1), where the areas marked in black represent the pores created after the electrochemical anodization process with sulphuric acid and the morphology of the analysed area shows a good pore dispersion.

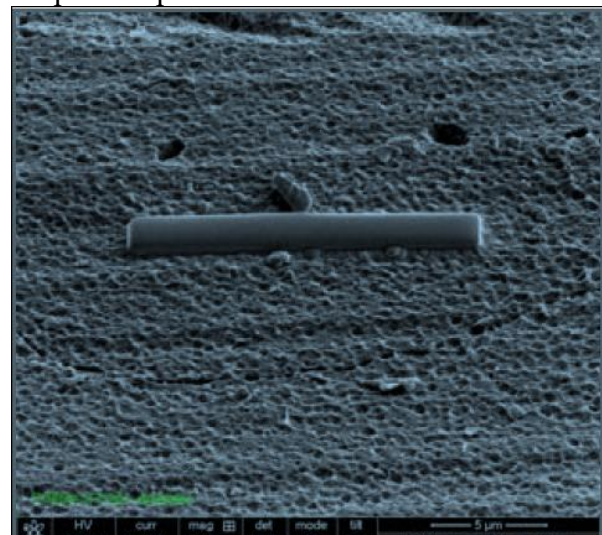


Figure 2. Anodic layer morphology and cut out area at magnification 5000X

By making a cut-out on the analysed area (Figure 2), the depth of aluminium oxide layer created after the anodizing process, can be observed.

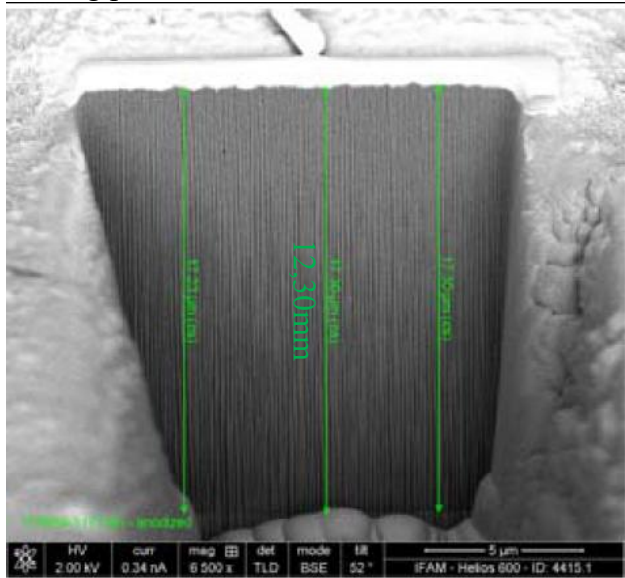


Figure 3. Cross section of anodic layer in cut out area

In addition, with the scanning electron microscope, the thickness of the anode layer can be measured (Figure 3).

In most cases, the anodizing treatment is followed by surface treatment, which is achieved by applying paint layers and are designed to create a system intended to protect the product during its life cycle.

3. SURFACE TREATMENT APPLICATION

In the recent period, water based paints have been used to apply surface treatments to components in the aeronautical industry. Water-based paints use water as solvent, which is more environmentally friendly than older solvent based paints (epoxy, etc.), which release a large amount of volatile organic compounds.

The application of water-based paints can be accomplished by several methods, such as:

- Brushing,
- Immersion,
- Spraying.

In the case of brush application, the result of application in most cases is anaesthetic. This type of application is limited to hard-to-reach areas or minor repairs.

Immersion, although seemingly fast enough, is limited by the requirements to use the paints once they have been mixed (a few hours). Thus, the tank of water-based paint needs to be drained frequently, resulting in a huge waste of water based paint.

Of the three application methods outlined above, spraying offers the optimal way of balancing costs,

product requirements (aesthetic appearance, layer thickness, etc.) and painting requirements (pot life).

Thus, spraying is done using a small amount of prepared paint, with a relatively small loss (generally caused by spraying adjacent to the product) allowing for efficient use.

On the other hand, the use of the spraying method has the following requirements on the preparation and the actual process:

- Components to be painted must be clean, free of dust contamination,
- The application temperature must be within 15-35 degrees Celsius,
- Humidity during application should be between 30 and 65%
- Application parameters to be constant:
 - Air pressure,
 - Application speed,
 - Distance between application gun and component,

In addition, in case of manual application, the following conditions are important:

- Light conditions in the application area,
- Ventilation system.

Surface treatment is generally carried out using two types of water-based paint. The first and most important, is the primer, which creates the adherent layer between the surface treatment and the base material, in the case of this paper, aluminium. For components in the aerospace industry, the primer layer should be between 15-25 microns and is generally green in colour.

Components that are installed in areas accessed by staff or passengers, usually receive a second layer of water-based paint that offers an aesthetic look. This layer of water-based paint has a thickness between 20-30 microns and requires extra attention during application, being the visible layer after the parts are installed on the aircraft [4].

4. ADHESION TESTING

A crucial factor in the life cycle of a component is the protection given by surface treatment, and for this protection to work, surface treatment needs to remain attached to the component. This feature is called adhesion of surface treatment to the material (aluminium).

In order to be able to test this product characteristic, after the production process, some samples are created, to which a destructive process is applied in order test the adhesion of the surface treatment. This

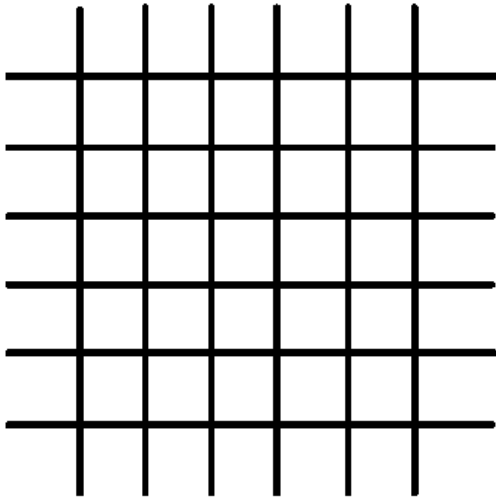
destructive process is called the "crosscut test" and is carried out according to the international ISO 2409 standard.

The crosscut test consists of cutting parallel horizontal lines and in a similar way, lines perpendicular to the horizontal ones, thus making a grid. Depending on the thickness of the surface treatment tested, the distance between the lines may differ, in the case of this paper the distance is 1 millimetre. To perform the crosscut test, a special tool is used for this application, and the user has to apply a force so that after performing the cross cut, the base material can be seen, in the cut area.

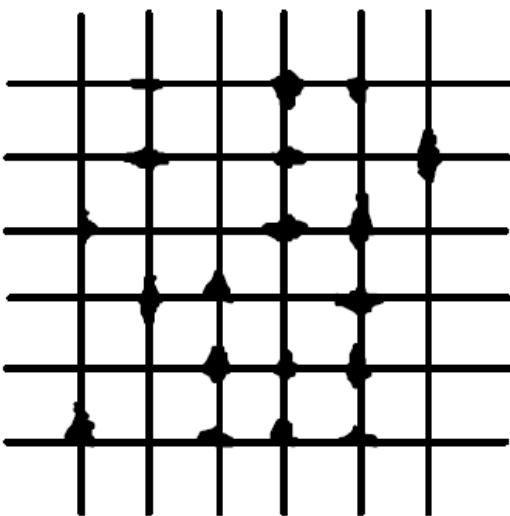
After the crosscut is made, the area is inspected and categorized according to the criteria given by international standard ISO 2409.

The possible results are:

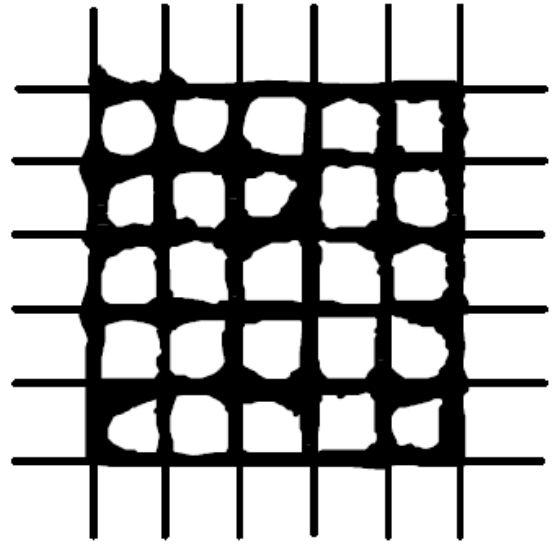
- GT0, considered optimal;



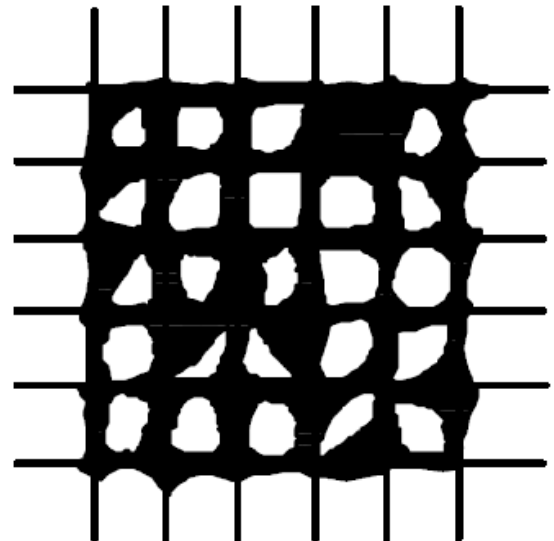
- GT1, small detachments of surface treatment in intersection zones and is considered acceptable;



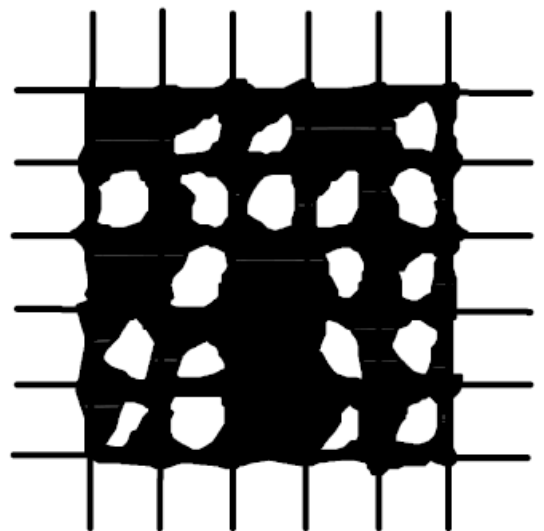
- GT2, detachment on the lengthwise of the surface treatment and is not considered acceptable;



- GT3, discontinuation of the surface treatment, including certain areas and is not considered acceptable;



- GT4, major discontinuation of the surface treatment and is not considered acceptable;



- GT5, complete discontinuation of treatment and is not considered acceptable [5].

5. CONCLUSIONS

To verify the influence of the electrochemical anodizing process with sulphuric acid, two sets of samples were created [6]:

a. The first set of samples was treated with the following processes:

- Pre-cleaning,
- Sulphuric acid anodizing,
- Water-based primer application,
- Water-based paint application.

b. The second set of samples was treated with the processes:

- Pre-cleaning,
- Water-based primer application,
- Water-based paint application.

After samples were tested using the crosscut test (according to ISO 2409) and the results were evaluated and categorized.

Adhesion for the set samples that were treated with the electrochemical anodizing process with sulphuric acid is clearly superior, with a GT0 result (Figure 4).

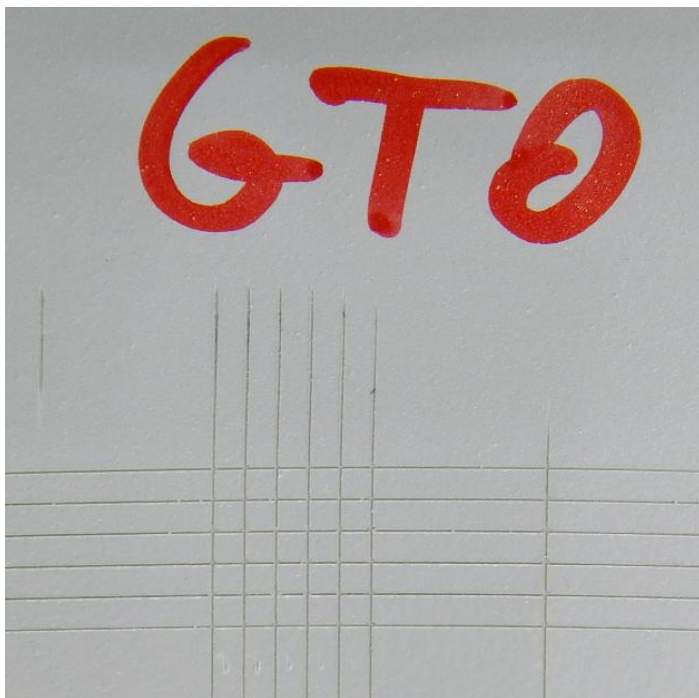


Figure 4. Cross cut result of first set of samples, treated with the electrochemical anodizing process with sulphuric acid

Compared to the set of non-anodized samples with a GT4, have an unacceptable result (Figure 5), according to the ISO 2409 criteria.

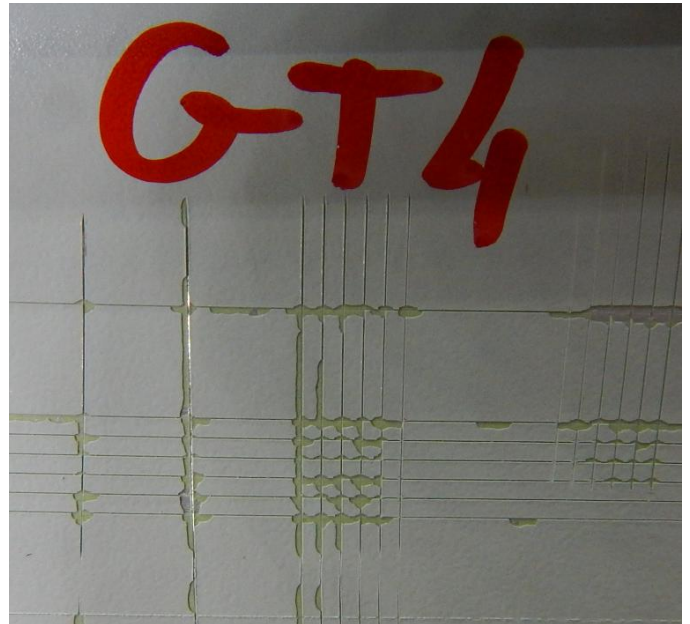


Figure 5. Cross cut result of second set of samples, treated without the electrochemical anodizing process with sulphuric acid

Although the samples from the second set were pre-cleaned prior to application of the surface treatment (primer and water-based paint), the adhesion result is poor, endangering the life cycle of the components treated in this way.

The combined application of the electrochemical anodization process with sulphuric acid and surface treatment (primer and water-based paint) offers the best adhesion result due to the porosity of the aluminium oxide layer and gives the component a prolonged life cycle.

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