

## **TALAT Lecture 5201**

# **Aluminium Surface Pretreatment**

12 pages

Level: Advanced I

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### **Objectives:**

- to give an overview of the various pretreatment methods prior to surface treatment of aluminium
- to learn about the important parameters and the mechanisms causing surface alterations

### **Prerequisites:**

- knowledge of the surface properties, the metallurgy and the electrochemistry of aluminium
- TALAT Lectures 5101, 5102, 5103, 5104, and 5105

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## Table of Contents

<b>5201 Aluminium Surface Pretreatment</b> .....	<b>2</b>
<b>5201.01 Introduction</b> .....	<b>3</b>
<b>5201.02 Mechanical Pretreatments</b> .....	<b>4</b>
<b>5201.03 Chemical and Electrochemical Polishing</b> .....	<b>5</b>
The Processes .....	5
Electropolishing .....	6
Description of the Different Electropolishing Processes .....	7
<i>Brytal Process</i> .....	7
<i>Alzak Process</i> .....	7
<i>Phosphoric Acid Processes</i> .....	7
Chemical Polishing .....	7
<b>5201.04 Chemical Cleaning</b> .....	<b>8</b>
Solvent Cleaning.....	9
Emulsion Cleaning.....	9
Vapour Degreasing .....	9
<b>5201.05 Chemical Etching</b> .....	<b>10</b>
Etch Cleaning Solutions.....	10
Matt Etching of Aluminium.....	11
<i>Alkaline Etching</i> .....	11
<i>Acid Etching</i> .....	12
<b>5201.06 Literature</b> .....	<b>12</b>

## 5201.01 Introduction

The appearance and the serviceability of an aluminium product depend to a great extent on surface treatments which precede the actual finish. Often problems occurring in the surface finish are related to a poor surface pretreatment. These pretreatments may be divided under three headings, according to whether they are mechanical or chemical or electrochemical in nature. The extent to which they are, respectively, used is dependent on the initial state of the surface, the method of manufacture of the article and the finish required. In this lecture an overview will be given of the various surface pretreatments. It is not the aim to treat in detail the exact process technology to perform the treatment. The information is more concentrated around the impact of the treatment on the aluminium surface, the important parameters and the mechanism which are leading to the necessary surface alterations.

Quite a number of treatments can be imposed, the selection of which is based on a number of criteria:

1. the original state of the Al surface
  - the selection of the Al-alloy
  - heat treatment
  - mechanical preparation (extrusion - rolling)
2. the type of surface treatment processing
  - batch process
  - continuous process
3. type of the article, required finish
4. cost, safety, ecology, etc..

No unique set of pretreatments is normally given for a required finish, often different combinations are possible to obtain a required finish.

## 5201.02 Mechanical Pretreatments

Mechanical pretreatments may be employed for different reasons. They can be tabulated as follows:

1. Mechanical treatment to eliminate scratches, pits or superficial blemishes and to provide a smooth lustrous surface. The aim of this treatment is thus to provide a flat surface. This aim is achieved by the various grinding and polishing operations which take off the high spots of a rough surface, either by a cutting action of the abrasive or by flowing the metal with the formation of a thin amorphous layer on the surface. With small articles, this process is often economically carried out by treating the work in quantity in polishing barrels. Mechanically polished surfaces are either left unprotected, as in aluminium kitchen ware, or may be lacquered, or anodized for improved corrosion resistance. Mechanical polishing is also employed prior to electroplating.
2. A second reason why mechanical polishing is used, is to prepare a rough surface with a certain pattern. The aim is to create a clean and rough surface, suitable for the direct application of paints and sprayed metal which shows good adhesion properties. Sand-, grit-, or shot-blasting are often used.
3. Mechanical treatments such as fluting, hammering, pattern rolling produce designs on the metal which may be subsequently lacquered or anodized, or partly or wholly painted or enamelled, according to the required finish.

## 5201.03 Chemical and Electrochemical Polishing

- The processes
- Electropolishing
- Chemical polishing

### The Processes

Chemical and electrochemical processes are employed in the production of smooth, bright surfaces. The function of this process can be compared with the mechanical polishing process. However, the principle by which polishing is carried out, is completely different. While mechanical polishing produces a flowed amorphous surface under the influence of pressure and local high temperatures, chemical and electrochemical polishing are selective dissolution processes by means of which the high spots of the rough surface are dissolved faster than the depressions. The advantages are:

- a) being similar in operation to anodizing and electroplating processes they can be employed together in a single production line,
- b) they are more suitable for bulk treatment and labour costs are much lower,
- c) the surface is relatively more clean.

Normally, the following objectives of the polishing processes can be distinguished:

- processes to replace mechanical polishing by use of high dissolution rates of 2,5-5  $\mu\text{m}$  per minute.
- processes employed after mechanical polishing. These processes have a low rate of attack and are employed e.g. on aluminium reflectors and other components which require a higher specular reflectivity than is obtained by mechanical methods alone. Their use is restricted to high-purity based materials since reflectivity falls off sharply when the quantity of second-phase constituents present increases.

A large number of electrolytic and chemical polishing processes have been developed to replace mechanical treatment. Mechanical polishing is characterized by high labour cost. The shape of the component is the largest single factor that determines whether automatic polishing machines are applicable or one has to resort to costly hand operations. The greatest savings are obtained by chemical and electrochemical polishing when the ratio of the functional surface area to be polished to the total component surface area is high.

Chemical treatments require no current and are, therefore, often less expensive than electropolishing, because the high current requirements of the latter involves considerable capital investment for rectifiers. However, this is offset to some extent by greater fume emission and extracting problems accompanying chemical brightening process. The fact that most electrolytic processes produce an oxide film which has to be

removed after brightening and before anodizing may also effect the choice of process to be used.

## **Electropolishing**

To understand electropolishing it is necessary to discuss the oxidation of aluminium in different electrolytes. This was already discussed in **TALAT Lecture 5102**. As was mentioned there, aluminium is subjected to oxidation reactions by a lot of aluminium surface treatments. The characteristics of the treatment are essentially determined by the chemistry of the solution. In the case of the electropolishing process the polarization of the aluminium and the attack of the solution are selected in such a way that a limiting oxide film is formed on the aluminium substrate. The actual dissolution rate and film thickness at which electropolishing takes place may vary widely.

The film which is formed on the aluminium substrate is of great importance as it avoids crystallographic etching. This is attributed to the substitution of dissolution of metal atoms according to their energy, i.e. the position they have in the crystal lattice, by the dissolution according to their access and the characteristics of the oxide layer. Under the conditions of electropolishing the dissolution is controlled by the slow diffusion of the reaction products away from the surface. With continuous film growth and dissolution the points of access where dissolution takes place are constantly changing and the metal atoms are, therefore, attacked more or less at random. By this action a smoothing of the surface is obtained. The efficiency with which etching is suppressed will vary with the thickness and porosity and electrical properties of the film. The film which is formed under electropolishing conditions is not qualitatively different from that produced in the anodizing process (see **TALAT Lecture 5203**). Film thickness and actual dissolution rate differ from process to process (thickness is about 0,5  $\mu\text{m}$ ).

Again, as in anodic oxide films formed in anodizing electrolytes, the film formed during electropolishing consists of hexagonal cells and both the cell and the pore diameters grow with the increasing potential. The theory of the porous film formation will be further discussed in the lecture related with the anodizing (**TALAT Lecture 5203**). Like in most other surface treatment processes the characteristics of the electropolishing and the characteristics of the film depend also on the purity and composition of the aluminium substrate.

Often a difference is made between electrobrightening and electropolishing:

In the first case the objective is to have a moderate smoothing action. The action is neither intense nor speedy. The process operates at low current densities of 300-500  $\text{A/m}^2$ , 2-12  $\mu\text{m}$  are removed, the typical duration time is between 20 to 30 min.

For electropolishing, however, the objective is to deal with abrasion and scratches on the surface. The electrochemical action is, therefore, more intense and necessitates higher current densities of the order of 1000-3500  $\text{A/m}^2$ . More metal is removed, 30-40  $\mu\text{m}$  in a few minutes.

## Description of the Different Electropolishing Processes

### *Brytal Process*

sodium carbonate 12-20 %  
trisodium phosphate 2.5-7.5 %  
temperature 75-90 °C  
voltage 7-16 V

Application: pure aluminium, especially used for reflectors for light and heating articles, badges, buttons and other decorative work.

### *Alzak Process*

fluoboric acid 2.5 %  
temperature 30 °C  
current density 1-2 A/dm<sup>2</sup>  
voltage 15-30 V  
operation time 5-10 min

Applications: reflectors

### *Phosphoric Acid Processes*

sulphuric acid 4-45 %  
phosphoric acid 40-80  
voltage 7-15 V  
current density 2.7-100 A/dm<sup>2</sup>  
temperature 70-95 °C  
operation time 20 min

Applications: used to replace mechanical polishing

## **Chemical Polishing**

The chemical process is more recent of origin. But, in fact, the theory or mechanism is nearly the same as for electropolishing. The external applied current is replaced by a chemical oxidizing agent. So the current is set by processes at the surface itself, under the influence of a powerful oxidizing agent, sometimes with the help of heavy metals deposited on the surface. Again a solid film is formed.

– Processes

Most of the solutions employed in industry for chemical polishing are based on a mixture of phosphoric acid and nitric acid or sulphuric acid.

## **5201.04 Chemical Cleaning**

- Solvent cleaning
- Emulsion cleaning
- Vapour degreasing

The cleaning of the aluminium substrate is very important as it is used for almost every type of metal finishing. Normally the aluminium surface is received relatively clean and free from many surface contaminations compared to many other metals. Nevertheless, the rolled surface may still be contaminated to a certain degree by oxides or airborne dirt impacted on the surface during the rolling stages which may be sufficient to interfere with subsequent surface treatments. Usually, therefore, a specific cleaning process must be carried out to provide a uniform chemically active surface. Other surface contaminations may occur originating from mechanical pretreatment in operations such as drilling, sawing, etc., where lubricants, grease and cooling liquids are often used. In particular cases a specific cleaning process must be carried out: certain alloyed sheets, such as those containing copper for high strength applications as used in air-craft industry, may have been given a protective coating of grease or lanolin to eliminate the possibility of surface corrosion during transit of location. These protectives must be removed before the final permanent surface treatments are applied.

So it can be concluded that if further surface treatments are to be carried out, in addition to the physical removal of oil etc., the surface must be chemically cleaned to remove oxides present on the surface by controlled etching of the surface which will provide a uniform base. Depending on the situation, a variety of methods are available, some of which are common to other metals, but in some cases there are specific variations. The method selected will depend upon a number of variants, these being:

- a) type of soil or contaminant
- b) end use of component, including subsequent processing
- c) cost
- d) health and safety

## **Solvent Cleaning**

The simplest but seldom the most effective way of removing grease or oil, is by wiping with a clean rag, moistened with an organic solvent. This method is commonly used for one-site cleaning and where the requirements for cleaning are not critical. Also such solvents are expensive and often a hazard to health, possibly a fire risk and causing pollution.

## **Emulsion Cleaning**

Emulsion cleaning consists of immersing components in a bath containing organic solvents and wetting agents added to a paraffin base. The aluminium is soaked in the mixture, allowing grease or oil to be loosened or removed, followed by one or two running water rinses to emulsify and remove any residual surface contaminants. However, it is not used so much anymore also due to the problems which can arise over treating emulsified effluent water.

## **Vapour Degreasing**

Aluminium components can be degreased by suspension in a vessel containing hot vapour from boiling organic solvents at the bottom of the tank. The cleaning action occurs mainly when the hot vapour condenses on aluminium which is cold when it is first immersed in this vapour, and the liquid drops down to the bottom of the tank taking with it oil or grease or other contaminations. The advantages are that the vapour and the condensed solvents are hot and an easy regeneration of the vapour solution is done by distillation. It is a useful method for cleaning oil or grease from small parts, this process, however, does not produce a chemically clean surface.

## 5201.05 Chemical Etching

- Etch cleaning solutions
- Matt etching of aluminium

The use of solvents for cleaning aluminium will only remove surface contaminants which are comparatively loose. This may be sufficient for some purposes, but where further processing is carried out, such as painting or anodising or plating, a chemically clean surface is necessary. In addition to contaminants, aluminium or magnesium oxides may be present on the surface in varying amounts or in different forms. These oxides have to be removed and replaced by a uniform oxide surface, otherwise they can produce variable and unpredicted responses to later surface treatments.

Chemical cleaning is more than simply freeing the surface of contaminants. In most cases it involves dissolving off the surface layers of aluminium, oxides, or heat treatment staining, by a small amount of etching and leaving the thin oxide coating normally present in a uniform condition. The selected method of cleaning will depend on three variables:

1. alloy or grade of aluminium
2. surface contaminant
3. subsequent processing

Examples for different cleaners are given below. However, etching of aluminium is a very specialized operation, and its success will determine the effectiveness of subsequent treatments. There are a number of proprietary cleaners made by suppliers which, in addition to the basic ingredients, contain a number of useful additives.

### Etch Cleaning Solutions

Most chemical cleaners for aluminium are alkaline and based on mixtures of caustic soda, tri-sodium phosphate and sodium carbonate. The caustic soda will saponify grease or lubricants from the aluminium surface, whilst at the time dissolving a small amount of aluminium, leaving a clean etched surface. The solutions are often inhibited to prevent excessive etching of the aluminium.

– De-smut solutions

If treatment in caustic soda etch solutions is longer than 30 s, a smut due to impurities or alloying elements is formed on the surface, which in most cases can be removed by a short dip in cold nitric acid.

– Acid cleaning

Acid cleaning is used for particular applications. Not so effective as alkali cleaners for removing grease or lubricants it finds favour in removing oxide films, which are often thickened during thermal treatment of aluminium. It is particularly effective in removing magnesium oxides found on components made from aluminium alloys. Acid cleaners usually contain sulphuric and phosphoric acid.

### **Matt Etching of Aluminium**

Important in this part is to realize that the aluminium surface can be changed in a number of ways to alter its appearance, ranging from a matt, diffuse finish (produced by etching) to one of bright mirror-like reflectivity (produced by brightening or polishing operations, see earlier). In this part we will concentrate upon the etching in order to produce a matt surface.

During manufacture, aluminium components may be superficially marked by the various processes such as blanking, forming, etc. as well as from the effects of rolling and extruding. In many cases this may not matter but often it may be desirable to remove or mask any rolling marks on sheet, abrasion or scuff marks or any other surface imperfections. Extrusions may also show a directional marking due to the extrusion process. The effects of these superficial defects can be overcome by etching the components in acid or alkaline solutions to produce frosted or diffuse surface which disguises any scratches or mechanical damage, eliminate glare from an originally bright rolled sheet or give a uniform, but matt appearance. By far the greatest proportion of etching is carried out as a pretreatment before anodising.

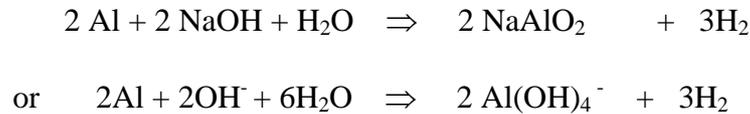
#### *Alkaline Etching*

Chemical etching can be carried out in a number of solutions but the simplest and cheapest form are alkaline solutions based on caustic soda. When aluminium is immersed in hot caustic soda the surface is progressively dissolved to form a finish which is microscopically roughened and on which a large number of small pits or depressions are developed. This produces a matt or dull appearance due to the scattering of reflected light. The final appearance will depend on the extent of etching and on the size and shape of the pits, as well as the contributions made by the aluminium, such as composition and methods of manufacture. A typical process: caustic soda 5 %, temperature 50-65 °C, time 10-20 minutes.

This type of etching solution often contains various additives, e.g. nitrites, fluorides, wetting agents etc., which modify the etching action. One of the problems in operating an alkaline etching process is the build up of scale on tank walls and heating coils. This causes the solution to saturate in dissolved aluminium which is eventually precipitated as alumina in the form of a rock-like deposit. This effect can be reduced by adding

chelating agents such as gluconates and heptonates to the etch solution.

The process is based on the amphoteric character of aluminium. Aluminium is oxidized to form aluminate anions. Hydrogen evolution takes also place



The deposition reaction is the following: the uncombined caustic soda precipitates as the reaction proceeds, a concentration of sodialuminate is built up. 1/4 free caustic soda must remain.



### *Acid Etching*

Etching in acids is not so frequently used, but under certain circumstances there are advantages. It is e.g. used in the case of a high silicon content, due to the fact that silicon is insoluble in caustic soda. A typical acid solution is composed of nitric and hydrofluoric acid.

Another important process in the electrograining process. This process is very important in the production of lithographic offset plates. The electrolytic etching is usually carried out in a dilute hydrochloric acid electrolyte (about 15 g/l) at temperatures of 230 °C using current densities of 500-3000 A/m<sup>2</sup>.

The process results in the formation of a heavily pitted, but very uniform, matt surface. This surface, where you want to have a finely textured matt etch with no directional effects or metallurgical features, is important in printing operations as it controls the hydrophilic behaviour of the plate.

## **5201.06 Literature**

WERNICK S., PINNER, R. and SHEASBY, P.G., "The Surface Treatment and Finishing of Aluminium and Its Alloys" 5th ed., ASM International, Teddington Vol 1, 1987

BRACE, A.W. and SHEASBY, P.G., "The Technology of Anodizing of Aluminium" Technicopy Limited, Glos 1978, p.39.

KING , R.G., "Surface Treatment and Finishing of Aluminium", Pergamon, Oxford, 1988.