

ANODISING OF ALUMINIUM

Anodising is a process for producing decorative and protective films on articles made of aluminium and its alloys. The article is made the anode of an electrolytic cell with aqueous sulfuric acid as electrolyte where the following overall oxidation reaction occurs.



A dense even layer of oxide about 0.08 μm thick is formed rapidly, followed much more slowly with a more porous layer up to 25 μm thick.

Before anodising the surface of the article must be thoroughly cleaned, normally using a detergent based process, and etched with a solution of sodium hydroxide.

After anodising the surface may be coloured with a dye or by an electrolytic method using appropriate metal cations, and then sealed by placing in boiling water, the pores in the oxide layer being closed off.

INTRODUCTION

Anodising is a process for producing decorative and protective films on articles made from aluminium and its alloys. It is essentially a process where a thick film of aluminium oxide is built up on the surface of the aluminium through the use of a direct current electrical supply. In the majority of anodising plants in New Zealand it is carried out in an electrolyte bath containing sulphuric acid with aluminium sheet cathodes and the work to be anodised attached to the anode (**Figure 1**).

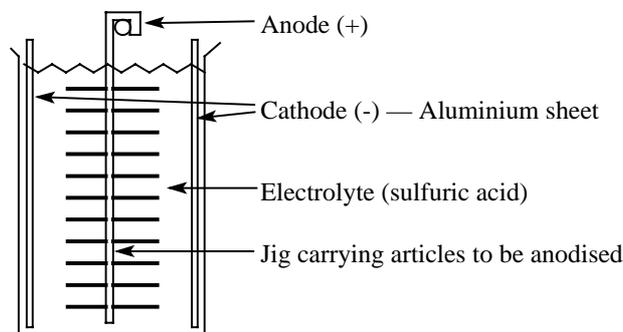


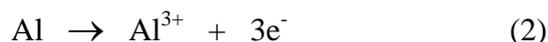
Figure 1 - A typical anodising cell
(Articles have to be securely fastened to ensure electrical contact during the anodising)

When the current is flowing in the cell the following sequence of events is believed to occur. Sulphuric acid begins to decompose, the hydrogen ions moving to the cathode where they are reduced to hydrogen gas:

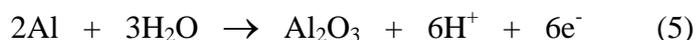


Simultaneously, negatively charged anions, i.e. hydroxide, sulphate and maybe oxide ions move to the anode. The electrical charge in the circuit causes positively charged aluminium ions (Al^{3+}) to be generated in the anode and in turn move toward the cathode. At the anode surface they react with the oxide/hydroxide ions to form aluminium oxide (in the case of the hydroxide ion, hydrogen ions are released into the solution).

Equations of the anode reactions



For which the overall process is:



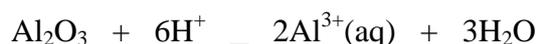
The sulphate ions also play some part as the oxide coating contains 12 - 15% sulphate ions. It is suggested that the sulphate ions facilitate the movement of hydrogen ions reducing the cell voltages required.

THE DEVELOPMENT OF THE ALUMINIUM OXIDE LAYER

Fresh aluminium reacts readily with oxygen to produce aluminium oxide. Once formed the oxide remains firmly bonded to the surface forming an impenetrable layer. Consequently, further reaction ceases. The film is very thin (0.01 μm), and despite its tenacity it can be removed by abrasion and chemical corrosion. In such instances the aluminium is subject to wear or the surface will mark or become pitted at the site of corrosion.

Anodising produces much thicker coatings (12 - 25 μm) which, if properly sealed, can extend the life of the surface appreciably. Recent research in New Zealand has shown that pitting of the surface can be reduced by up to 90% with a 12 μm coating, and by up to 93% with a 25 μm coating.

In the initial stages (i.e. first 60 s) of anodising the oxide layer formed is dense and of even consistency. It provides the greatest resistance to wear and corrosion and consequently is called the barrier layer. The growth of this layer ceases when the high electrical resistance of the oxide reduces the potential of the applied voltage in the electrolytic cell. The depth of the coating at this stage is about 0.08 μm . Subsequent growth is very slow and competes with the acid reaction:



which releases Al^{3+} ions into the solution. Note that the H^+ can be at high concentration near the oxide layer due to one of the anode reactions above. See equation (5).

At low applied voltages only the barrier layer forms. However, the gradual production of Al^{3+} ions tends to smooth out the underlying metal surface and give a brightening effect to the article. Objects such as wheel trims and bumper bars are generally treated in this way.

At higher voltages the growth of the layer continues beyond the barrier layer. Unlike the initial barrier layer this secondary layer, although constitutionally the same, has an open pore-like structure; a consequence of the competing anodising and acid solution processes. Electron photomicrographs reveal the structure of these anodised surfaces to be as shown in **Figure 2**.

The conditions required to produce coatings vary according to the concentration and nature of the electrolyte, the voltage - current density applied, the alloy being anodised and the temperature of the bath. In the majority of electrolytic plants articles are anodised at a potential of 15 - 20 V and a current density around 1.6 $\text{A d}^{-1} \text{m}^{-2}$; the electrolyte is 3.5 mol L^{-1} sulfuric acid maintained at temperatures between 20 and 23°C. Under these conditions the

quality of the coating is satisfactory for most applications. At higher electrolyte concentrations and temperatures, and at lower voltages or current densities, the acid solution process occurs earlier in the development producing thin, open oxide coatings. Conversely, hard dense coatings are produced at low temperatures and high current densities. The conditions established in each plant are determined by the type of application.

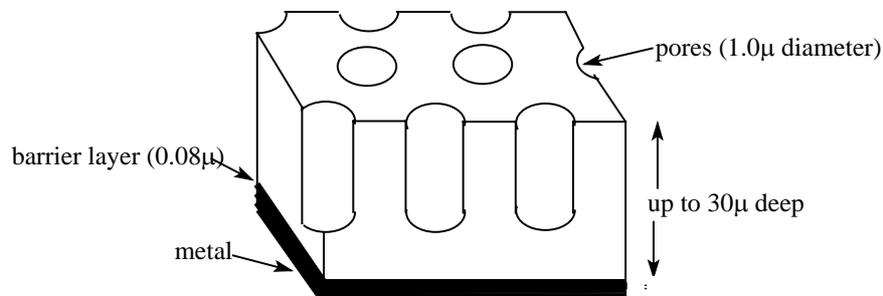


Figure 2 - Structure of anode layer

Table 1 - Applications of anodised articles and conditions required

Application	Film type	Thickness / μm	Electrolyte
Capacitors - very thin layers of aluminium oxide coating	Barrier	0.01 - 0.5	boric acid, ammonium tartrate
Architectural (silver look)	Sealed, porous	10 - 25	sulfuric acid
Architectural (coloured)	Electrolytically coloured porous coat, sealed	10 - 20	sulfuric acid
Very durable engineering applications	Hard anodising	50 - 120	sulfuric acid, high current density

The suitability of common aluminium alloys to be anodised is summarised in **Table 2** below.

PRE-TREATMENT

Step 1 - Cleaning

Correct and adequate cleaning of the aluminium object prior to anodising is essential if the finished work is to have a uniform and attractive appearance. When aluminium arrives from the rolling, casting or extrusion mills it may be soiled in one or more of the following ways:

Table 2 - Aluminium alloys in New Zealand

Alloy	Components	Characteristics	Anodising suitability
Pure	99.99 % Al	Soft, non-commercial	Excellent
6063	0.3 - 0.6 % Si 0.35 % Fe 0.45 - 0.9 % Mg balance Al	General purpose extrusion	Good for general anodising and colouring
6351	0.7 - 1.4 % Si 0.5 % Fe 0.4 - 0.8 % Mg balance Al	Extrusion alloy High tensile strength	Not usually anodised
5251	2 % Mg balance Al		Satisfactory
3203	1 % Mn trace Fe/Si as impurities balance Al	Sheet rolled	Not recommended for anodising
1200	0.4 % Fe 0.2 % Si 99.4 % Al	General purpose Sheet rolling	Anodises well

- Carbonaceous deposits from the surface of forgings and die castings
- Traces of oil-based lubricants
- Traces of polishing compounds or sanding grits
- Oxide films from heat treatment

Cleaning these 'soils' from the surface may prove difficult, especially if the requirements of the work do not allow etching of the surface. Most cleaning solutions used in New Zealand operations are detergent based. In addition to the detergent, a wetting agent and a complexing compound may be used. The complexing compound frequently used is sodium polyphosphate - a component of many soap formulations - which prevents ions, such as Fe³⁺, adhering to the surface of the work. If etching is not a problem, sodium hydroxide or sodium carbonates (Na₂CO₃ / NaHCO₃) may be added to increase the effectiveness of the solution.

Step 2 - Etching

Etching is most often achieved by the use of a warm, 10 % (2.5 mol L⁻¹) sodium hydroxide solution. It gives the surface of the metal a light grey satin finish (through diffuse reflection of the incident light). The vast majority of work is pretreated in this way. In theory the reactions occurring in the etching solution are:

- The etching reaction:



- Dissolution of the aluminate:

$$\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al}(\text{OH})_3 \quad (8)$$
- Dehydration of the solid hydroxide:

$$2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$

The rate of etching is dependent on the concentration of the sodium hydroxide solution, the temperature and the concentration of aluminium ions which are released into the solution. When high concentrations of aluminium ions are present the solution loses its effectiveness. Presence of other ions, some of which may be a component in the alloy, can also interfere in the process, causing blemishes to appear on the surface of the work.

The problem of ion contamination is overcome by employing etching solutions which suppress the action of the Al^{3+} and other metal ions released. The composition of these solutions are the propriety of the companies that develop them, but generally contain sequestering agents which complex metal ions. Such solutions do not have an infinite capacity to do this but, due to the 'carryover' of solution by the etched work and periodic replacement by fresh etch solution, the etching batch is maintained in an effective condition (**Figure 3**).

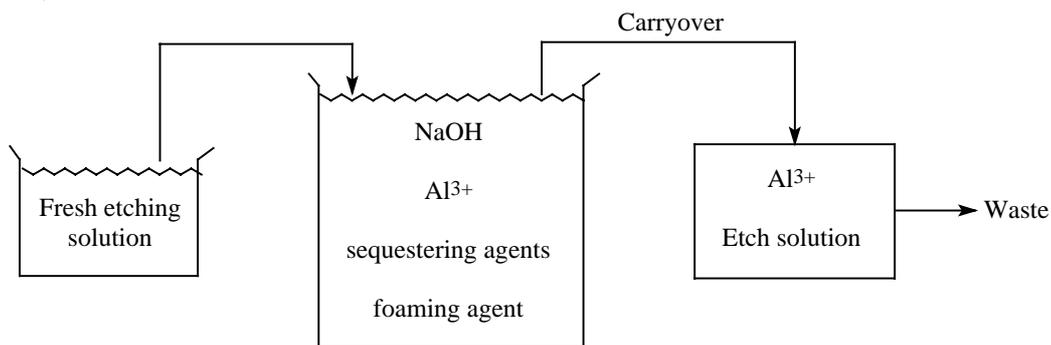


Figure 3 - The etching solution cycle

Foaming agents are also a constituent of the etching solution; their action is to reduce the pungent mists/fumes that result from the vigorous reactions that occur.

It is important to note that the appearance of the end result is determined at this stage. Work which is poorly etched will reveal scratches or blemishes no matter how well it is anodised or coloured.

POST TREATMENT

After cleaning and anodising the work is coloured and sealed. As all anodised work is sealed, sealing will be considered first, although if colouring is to be done it is carried out prior to sealing.

Sealing

Sealing is the process in which the pores at the surface of the oxide layer are closed off. It is effected by placing the anodised object in boiling water for a 15 - 20 minute period. During

that time the water reacts with the aluminium oxide to produce the mineral Boehmite - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{AlO} \cdot \text{OH}$:



Boehmite is a hard, transparent material with a greater volume than the aluminium oxide. As it forms it closes off the openings of the pores.

As would be expected, the durability of the anodised surface, especially in regard to chemical corrosion, is greatly influenced by the effectiveness of the sealing. If the duration of the sealing is too short the pores, although constricted, remain open for corrosion agents to be in close proximity to the aluminium surface. Corrosion studies have shown that anodised aluminium which has been sealed for 15 minutes or more has greatly increased resistance to pitting by chemical corrosion agents such as H^+ and Cl^- .

Colouring

Colouring involves the absorption of a coloured dye into the pores of the oxide coating which becomes fixed after the sealing process has been completed. Dyestuffs which can bond to the oxide or metal ions in the anodised layer have better colour properties than those that do not.

Electrolytic colouring is the most important method of colouring anodised aluminium today. It produces attractive finishes of very great colour and heat fastness and is easy to perform. The anodised work is dipped in a tank containing coloured ions of other metals. Although the constitution of the solutions are patent, typical examples of the processes are given in **Table 3** below.

Table 3 - Typical conditions for colouring anodised aluminium (all at room temperature)

Composition	Concentration/ g L^{-1}	Voltage	Time	Colour
CoSO₄ H₃BO₃ (NH₄)₂SO₄	20 25 15	15 V ac	10 min.	Bronze - Black
NiSO₄ H₃BO₃ Others	30 - 170 25 - 40	15 - 30 V ac	30 min.	Bronze
SnSO₄ H₂SO₄ Others	5 - 20 5 - 50	15 - 30 V ac	2 - 10 min.	Bronze - Black

Under the influence of alternating current the colouring agents deposit rapidly at the very base of the pores and the take is even over the entire surface. Unlike the process of dye absorption, electrolytic colouring is easy to control and gives uniformity of colour from one run to the next. The success of this technique is evident in the widespread use of bronze coloured aluminium in joinery and house fittings. Approximately 66% of all bronze tinted aluminium is coloured by this technique.

To a much lesser extent coloured inorganic compounds can be used to colour the work. Ammonium ferric oxalate is a very common compound used to impart a goldy colour to the metal. Other colours can be imparted by treating the absorbed ferric ammonium oxalate with

other compounds: for example, potassium ferrocyanide solution will react with the ferrioxalate compound to produce a blue colour. The technique used is to dip the work firstly in a solution of the ammonium ferrioxalate followed by dipping the work in the potassium ferrocyanide solution. This double dipping technique can be used with other compounds to produce a variety of colours: e.g. copper sulphate followed by ammonium sulphide gives green, and lead nitrate followed by potassium chromate gives yellow.

CONCLUSION

This is a brief overview of the chemistry of the anodising process. In industry the process can encounter many difficulties if care is not taken to ensure that solutions are controlled with regard to concentration and temperature. Thorough rinsing of the work is carried out after each stage to ensure that it enters the next process in the correct state. It also ensures that contamination of solutions from one stage by the preceding stage is kept to a minimum.

A further aspect of the industry not covered herein is that of quality control. Even in small plants chemists are employed to constantly check the conditions of the solutions and make recommendations / adjustments. In addition, frequent checks are made on the thickness of the film, its density and the colour quality.

Written by Geoff Groves (Ellesmere College) with reference to:

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- Fahy, F.W.; *Anodised Aluminium - Its Assessment by Accelerated Corrosion*; Paper presented at Symposium of Anodised Aluminium, 15th February 1979
- Hsieh An Kong, S.; *Colouring Anodised Aluminium - A Review*; Metal Finishing; October 1981
- Wright, G.A.; *Recent Research on Anodic Films on Aluminium*; Paper presented at Symposium on Anodised Aluminium; 15th February 1979