

Anodising



History

Oxalic acid anodising was first patented in Japan in 1923 and later widely used in Germany by companies such as Junkers on duralumin aircraft parts and for architectural applications.

Variations of this process soon evolved, and the first sulphuric acid anodising process was patented by Gower and O'Brien in 1927. Sulphuric acid soon became and remains the most common anodising electrolyte.

The phosphoric acid processes are the most recent major development, so far only used as pre-treatments for adhesives or organic paints. A wide variety of proprietary and increasingly complex variations of all these anodising processes continue to be developed by industry, so the growing trend in military and industrial standards is to classify by coating properties rather than by process chemistry.

Anodising changes the microscopic texture of the surface and changes the crystal structure of the metal near the surface. Thick coatings are normally porous, so a sealing process is often needed to achieve corrosion resistance. Anodised aluminium surfaces, for example, are harder than aluminium but have low to moderate wear resistance that can be improved with increasing thickness or by applying suitable sealing substances. Anodic films are generally much stronger and more adherent than most types of paint and metal plating, but also more brittle. This makes them less likely to crack and peel from ageing and wear, but more susceptible to cracking from thermal stress.

Anodising Aluminium

Anochrome carry out mainly Hard Anodising, however to understand what this is, it is worth looking at the whole principle of anodising.

Pure Aluminium, when exposed to oxygen or air at room temperature, self-passivates by forming a surface layer of

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amorphous aluminium oxide 2 to 3 nm thick, this is a natural formation AL_2O_3 , which by itself, provides a very effective barrier against corrosion. Pure aluminium is rarely used, but alloys of aluminium, copper, iron and silicon that form the majority of material used today, frequently referred to as 'aluminium' still produce a self passivated layer which tends to be thicker 5-15 nm but has flaws which leads to a reduction in corrosion resistance.

The Aluminium alloys are anodised to increase this naturally forming oxide layer in a controlled manner to give differing thicknesses depending upon the application of the component. Once anodised the micro pores on the surface can hold and retain lubricants, dyes and other sealants to further enhance the product. The surface once anodised will be harder than non anodised aluminium but will have moderate wear resistance on thin anodised films.

Other additional features of anodising, with the formation of aluminium oxides, is the improvement in the thermal resistance of the surface, the melting point of aluminium oxide is 2050oc which is much higher than of pure Aluminium at 658oc. There is a drawback with Anodised coatings, this is more relevant on some alloys than others, but with the films having a much lower thermal conductivity and coefficient of linear expansion than aluminium, the result is the coating will crack from thermal stress if exposed to temperatures above 80 °C. It will however not peel.

As Anodic film builds up both from the original surface and down into the surface by equal amounts, the resultant film therefore increases a linear part dimension by half the film thickness. A further example is with a piston bore diameter which will reduce by half the film thickness per side, i.e. the diameter will decrease on a component anodised to a 30um film thickness, decreasing by 30um.



Process

Before anodising is started the components are cleaned in a hot soak tank. They may require a surface etch in a sodium hydroxide solution, with additional additives such as Anodol, for a few seconds possibly up to one minute. Following this the parts will, if etched, need a de-smut wash for a minute or so to remove the residue left from the etching.



The anodised aluminium layer is grown by passing a direct current through an electrolytic solution- Sulphuric acid in Anochrome's case- with the aluminium component acting as the anode (positive). The current, which again varies depending upon the alloy type, amount of components being anodised and the part of the anodising cycle reached, releases hydrogen at the cathode (electrode) and oxygen at the surface of the aluminium anode, creating a build-up of aluminium oxide.

As the process continues, the presence of the component being within an acid solution slowly dissolves the aluminium oxide. The rate of dissolving is balanced by the rate of growth, and the resultant layers which contain Nano pores, 10-150 nm in diameter, are what allows the electrolyte solution and current to reach the aluminium thus continue growing the coating to greater thicknesses beyond what is produced by auto passivation. It is these pores that are later sealed or contain colour.



The thicker films also require tight temperature controlling of the electrolyte solution, to prevent the rate of film growth being exceeded by the rate of acid attack from the sulphuric acid in the anodising electrolyte. The rate of attack increases with temperature.

The anodised layer is built up from the base by the nascent oxygen produced by the direct current in the acid electrolyte. Half the aluminium oxide film is produced is dissolved by the acid electrolyte, the rest of the Aluminium oxide increases the film thickness.

Decorative anodised parts have a larger pore or cell structure compared to hard anodised parts. The cell walls are proportional to the voltage applied.

The size of the pore will depend on:

1. Solution Concentration.
2. Solution Temperature.
3. Current Density.

Higher solution concentrations and temperatures give higher pore sizes, which are good for dyes

Lower concentrations and temperatures give smaller pore sizes and thicker harder coatings. Higher current densities give thicker films and cooling is necessary to keep the temperature constant.

The film thickness can range from under 0.5 micrometres for bright decorative work up to 150 micrometres for architectural applications.

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The most widely used anodising specification, MIL-A-8625, defines three types of aluminium anodising. Type I is Chromic Acid Anodising, Type II is Sulphuric Acid Anodising and Type III is Sulphuric acid hard anodising.

Standards for hard anodising are given by MIL-A-8625 Type III, AMS 2469, BS 5599, BS EN 2536, type2 BS EN 212373-1 (which replaces BS1615) and the obsolete AMS 2468 and DEF STAN 03-26/1.

It is worth noting that in general the anodising specifications define tests and end process quality assurance methods rather than process chemistry.

Sulphuric acid types II and III are the most widely used solutions to produce anodised coating. Coatings in the range 1.8 to 25 μm (0.00007" to 0.001") are known as Type II (mainly due to MIL specifications in the USA), while coatings thicker than 25 μm (0.001") are known as Type III, or hard anodising.

Dyes and Colours

Sulphuric acid anodising produces a porous surface which can easily accept dyes, the larger the pore the better the dye will take. The range of colours is huge, however alloy choice will limit some of the colours, and hard anodise film tend to be a dark grey colour which will limit the choice even more.

It is worth remembering that the surface finish of the component before anodising and the amount of etching and de-smutting will have an effect on the brightness of the coloured film at the end of the process, castings particular can be difficult and lead to patchy finishes.

In general the surface finish of the part will not improve by hard anodising in fact the surface roughness is more likely to double during processing.

Organic pigments are the most cost effective but do not have the same colourfast stability and performance in sunlight than



that of the more expensive inorganic systems. They also have a ceiling of around 150°C before the pigment starts to break down.

More lightfast systems are available with inorganic systems which are electrolytically deposited, these are considerably



more expensive to apply.

A third method of colouring is to introduce the colour within the anodic film; here organic acids are mixed with the electrolyte. This process is limited to use on high volume bespoke lines where the need to change to a clean or alternative colour is not required.

Sealing

Any recently anodised aluminium substrates will have a porous surface to the anodic film, these pores at this stage absorb any colouring or lubricants. The larger the pore size the more important it is to seal. The time taken to seal a part is roughly equivalent to the time taken to anodise. If no additional requirements are specified the surface can be left and allowed to seal naturally over time or can be sealed.

Sealing can be accomplished in a number of ways, the simplest being a hot de-min dip which converts the oxides into its hydrated form, the resultant swelling fills the surface pores, this method does have a downside in that it reduces the abrasion resistance slightly.

A second method is cold sealing. Here the pores are filled with a nickel solution, this has the added advantage of significantly reducing energy costs compared to hot sealing and does not produce a seal smut.

The downside being the part must be dry before handling.

The third method of seal is a hot sodium or potassium dichromate seal; this does leave a slight yellowish colour on the part. Additional materials can be added to a seal such as PTFE, typically parts are also printed before sealing to stop any dye bleed out. Processes such as silkscreen, sublimation transfer or digital printer are frequently used.

Environmental

Anodising is one of the more environmentally-friendly metal finishing processes. With the exception of organic (aka integral colour) anodising, the by-products do not contain heavy metals, halogens or volatiles. The most common anodizing effluents, aluminium hydroxide and aluminium sulphate, are recycled through our in house effluent plants.

Information presented in this data sheet is considered reliable, but conditions and methods of use, which are beyond our control, may modify results. Before these product are used, the user should confirm their suitability.

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