

## ***What Is Anodising or Anodizing?***

Anodising is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called anodising because the part to be treated forms the anode electrode of an electrical circuit. Anodising increases corrosion resistance and wear resistance, and provides better adhesion for paint primers and glues than bare metal. Anodic films can also be used for a number of cosmetic effects, either with thick porous coatings that can absorb dyes or with thin transparent coatings that add interference effects to reflected light. Anodising is also used to prevent galling of threaded components and to make dielectric films for electrolytic capacitors. Anodic films are most commonly applied to protect aluminium alloys, although processes also exist for titanium, zinc, magnesium, niobium, and tantalum. This process is not a useful treatment for iron or carbon steel because these metals exfoliate when oxidised; i.e. the iron oxide (also known as rust) flakes off, constantly exposing the underlying metal to corrosion.

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 aging and wear, but more susceptible to cracking from thermal stress.

Preceding the anodising process, wrought alloys are cleaned in either a hot soak cleaner or in a solvent bath and may be etched in sodium hydroxide (normally with added sodium gluconate), ammonium bifluoride or brightened in a mix of acids. Cast alloys are normally best just cleaned due to the presence of intermetallic substances unless they are a high purity alloy such as LM0.

The anodised aluminium layer is grown by passing a direct current through an electrolytic solution, with the aluminium object serving as the anode (the positive electrode). The current releases hydrogen at the cathode (the negative electrode) and oxygen at the surface of the aluminium anode, creating a build-up of aluminium oxide. Alternating current and pulsed current is also possible but rarely used. The voltage required by various solutions may range from 1 to 300 V DC, although most fall in the range of 15 to 21 V. Higher voltages are typically required for thicker coatings formed in sulphuric and organic acid. The anodising current varies with the area of aluminium being anodised, and typically ranges from 0.3 to 3 amperes of current per square decimetre (20 to 200 mA/in<sup>2</sup>).

Aluminium anodising is usually performed in an acid solution which slowly dissolves the aluminium oxide. The acid action is balanced with the oxidation rate to form a coating with nanopores, 10-150 nm in diameter. These pores are what allow the electrolyte solution and current to reach the aluminium substrate and continue growing the coating to greater thickness beyond what is produced by auto-passivation. However, these same pores will later permit air or water to reach the

substrate and initiate corrosion if not sealed. They are often filled with coloured dyes and/or corrosion inhibitors before sealing. Because the dye is only superficial, the underlying oxide may continue to provide corrosion protection even if minor wear and scratches may break through the dyed layer.

Conditions such as electrolyte concentration, acidity, solution temperature, and current must be controlled to allow the formation of a consistent oxide layer. Harder, thicker films tend to be produced by more dilute solutions at lower temperatures with higher voltages and currents. The film thickness can range from under 0.5 micrometers for bright decorative work up to 150 micrometers for architectural applications.

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 coat anodising. Other anodising specifications include MIL-A-63576, AMS 2469, AMS 2470, AMS 2471, AMS 2472, AMS 2482, ASTM B580, ASTM D3933, ISO 10074 and BS 5599. AMS 2468 is obsolete. None of these specifications define a detailed process or chemistry, but rather a set of tests and quality assurance measures which the anodised product must meet. BS 1615 provides guidance in the selection of alloys for anodising. For British defence work, a detailed chromic and sulphuric anodising processes are described by DEF STAN 03-24/3 and DEF STAN 03-25/3 respectively.

### ***Chromic acid anodising (Type I)***

The oldest anodising process uses chromic acid. It is widely known as the Bengough-Stuart process. In North America it is known as Type I because it is so designated by the MIL-A-8625 standard, but it is also covered by AMS 2470 and MIL-A-8625 Type IB. In the UK it is normally specified as Def Stan 03/24 and used in areas that are prone to come into contact with propellants etc. There are also Boeing and Airbus standards. Chromic acid produces thinner, 0.5  $\mu\text{m}$  to 18  $\mu\text{m}$  (0.00002" to 0.0007") more opaque films that are softer, ductile, and to a degree self-healing. They are harder to dye and may be applied as a pre-treatment before painting. The method of film formation is different from using sulphuric acid in that the voltage is ramped up through the process cycle.

### ***Sulphuric acid anodising (Type II & III)***

Sulphuric acid is the most widely used solution to produce anodised coating. Coatings of moderate thickness 1.8  $\mu\text{m}$  to 25  $\mu\text{m}$  (0.00007" to 0.001") are known as Type II in North America, as named by MIL-A-8625, while coatings thicker than 25  $\mu\text{m}$  (0.001") are known as Type III, hard coat, hard anodising, or engineered anodising. Very thin coatings similar to those produced by chromic anodising are known as Type IIB. Thick coatings require more process control, and are produced in a refrigerated tank near the freezing point of water with higher voltages than the thinner coatings. Hard anodising can be made between 13 and 150  $\mu\text{m}$  (0.0005" to 0.006") thick. Anodising

thickness increases wear resistance, corrosion resistance, ability to retain lubricants and PTFE coatings, and electrical and thermal insulation. Standards for thin (Soft/Standard) sulphuric anodising are given by MIL-A-8625 Types II and IIB, AMS 2471 (undyed), and AMS 2472 (dyed), BS EN ISO 12373/1 (decorative), BS EN 3987 (Architectural) . Standards for thick sulphuric anodising are given by MIL-A-8625 Type III, AMS 2469, BS 5599, BS EN 2536 and the obsolete AMS 2468 and DEF STAN 03-26/1.

### ***Organic acid anodising***

Anodising can produce yellowish integral colours without dyes if it is carried out in weak acids with high voltages, high current densities, and strong refrigeration. Shades of colour are restricted to a range which includes pale yellow, gold, deep bronze, brown, grey, and black. Some advanced variations can produce a white coating with 80% reflectivity. The shade of colour produced is sensitive to variations in the metallurgy of the underlying alloy and cannot be reproduced consistently.

Anodising in some organic acids, for example Malic Acid, can enter a 'runaway' situation, in which the current drives the acid to attack the aluminium far more aggressively than normal, resulting in huge pits and scarring. Also, if the current or voltage is driven too high, 'burning' can set in; in this case the supplies act as if nearly shorted and large, uneven and amorphous black regions develop.

Integral colour anodising is generally done with organic acids, but the same effect has been produced in laboratory with very dilute sulphuric acid. Integral colour anodising was originally performed with oxalic acid, but sulfonated aromatic compounds containing oxygen, particularly sulfosalicylic acid, have been more common since the 1960s. Thicknesses up to 50µm can be achieved. Organic acid anodising is called Type IC by MIL-A-8625.

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