"The Behaviour Of The Aluminium Pore In Anodizing Depending On The Electrolyte, Current Density & Time Agitation Of Micro Bubble"

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Anodizing is an oxidation and hydration process as a result of which bohemite, $Ab_{2}O_{3} \times H_{2}O$, x=(1.3 - 1.7) is formed. The pores model achieved is identified with the Alcoa's known model in the shape of a hexagonal cell. On this work it is important to observe how the porous coating, non-porous coating and barrier coating behave depending on electrolytes, current density, time and micro-bubble agitation. Sulphuric, oxalic and malonic acids are used as electrolytes. We want to experiment and study how the new electrolytes can replace the sulphuric, phosphoric and chromic electrolytes. This implies researching on the new electrolytes for application on the food, precision mechanics and aerospace industries. This work is done under the auspices of the CSIC (Spanish High Centre of Scientific Research), Centre of Study and New Technologies of the Polytechnic University of Barcelona, and Centre for the Enterprises and Environment-CEMA. The work will have a duration of approximately three years.

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Principles of Anodizing

The manner in which anodic oxidation differs essentially from the industrial electrolytic processes will be apparent from the following three examples all using sulphuric acid, say 10% by volume, as the electrolyte.

In Figure A, if the electrodes are made of platinum or any other metal that does not dissolve at the anode or positive electrode, oxygen gas is liberated at the anode and hydrogen gas at the cathode. No metal is dissolved in the acid.



Figure A, Current Entering and Leaving Solution in Anodizing

If the anode is made of copper it will dissolve in the acid and will be re-deposited on the cathode. This is the basis of many metal electrodeposition processes. In commercial production with soluble metal anodes little or no gas is evolved at the anode and cathode.

When the anode is aluminium, the cathode, in commercial practice, is either aluminium or lead. When current is passed the aluminium anode does not dissolve away like copper, nor is oxygen evolved in quantity. Instead, most of the oxygen that would have been liberated combines with the aluminium to form a layer of porous aluminium oxide. Hydrogen is liberated at the cathode.

The amount of aluminium oxide formed is directly proportional to the current density and time, i.e. to the quantity of electric current used. The progress of the formation of the anodic coating depends upon the chemical composition of anodising electrolyte and the chosen conditions of electrolysis. Some anodising electrolytes have little or no solvent action on the oxide coating so that the process soon ceases, leaving a thin film usually referred to as a barrier-layer-type coating, the thickness of which is solely governed by the applied voltage and approximates to $1/700 \mu m$ per volt. This type of coating is typically produced in solution of borates, boric acid or tartrates.

If the electrolyte has some solvent action, then a porous film is formed and the oxidation process can continue leading to the production of relatively thick films, as for example in sulphuric acid. Eventually the rate of film formation is balanced by the rate of solvent attack, but this stage of the process is avoided in commercial practice.



Figure B. Microstructure of Anodic Film

The structure of the porous type of anodic oxide coating is shown diagrammatically in figure B, and can be seen to comprise hexagonal columns each with a central pore which reaches down to a thin compact barrier layer which is continuously formed and transformed into the porous form during the process.

The diameter of the pores and the thickness of the barrier layer for any given electrolyte and temperature are proportional to the applied voltage. Thus by varying the anodising conditions it is possible to alter the physical properties of the coating, such as the hardness, abrasion resistance and the density.

From the foregoing it will be appreciated that anodising is a conversion process so that the appearance and other properties are completely dependent upon the composition of the aluminium and its surface condition. Anodizing, therefore, differs fundamentally from processes such as electroplating where a layer of metal is applied over the base metal surface.

After anodising the film is usually sealed by a hydration process to minimize the initial porosity. For some special applications physical sealing with an organic material such as oil, is desirable. Colouring by immersion in dye solution is carried out after anodising but before sealing.

With aluminium alloys the alloying constituents are differently affected by the anodising process, and in turn influence the appearance and structure of the coating.

The properties of the coatings can also be modified by chemical additions to the electrolyte which is also sensitive to certain adventitious and undesirable impurities.

Material	Suitability for anodizing			Material	Suitability for anodizing				
designation & temper	Protective	Colour	Bright	Hard*	Iard* designation & temper		Colour	Bright	Hard*
1080A-0 1080-H8	E E	E E	V-E V-E	E E	5005-0 5005-H4 5005-H8	E E E	E E E	E E E	E E E
1050-0 1050-H8	E E	E E	V V		5083-0 5083-H2 5083-H4	V V V	V V V	G G G	E E E
1200-0 1200-H4 1200-H8	V V V	V V V	G G G		5154A-0 5154-H2 5154-H4	V V V	V V V	G G G	E E E
2011-TD 2011-TF	F F	F (D) F (D)	U U		5251-0 5251-H3 5251-H6	V V V	V V V	G-V G-V G-V	E E E
2014A-TB 2014-TF	F F	F (D) F (D)	U U		5454-0 5454-H2 5454-H4	V V V	V V V	G G G	E E E
2024-TB 2024-TD	F F	F (D) F (D)	U U		6061-TB 6061-TF	G G	G G	F F	V V
2618A-TF	F	F	U		6063-TB 6063-TF	V V	V V	G-V G-V	E E
3103-0 3103-H4 3103-H8	G G G	G G G	P-F P-F P-F		6082-TB 6082-TF	G G	G G	F F	G-V G-V
3105-0 3105-H4 3105-H8	G G G	G G G	P-F P-F P-F		7020-TB 7020-TF	F F	F F	*** ***	G G
					7075-TF	F	F	***	F

TABLE 1 - ANODIZING CHARACTERISTICS OF WROUGHT ALUMINIUM

E = Excellent / V = Very good / G = Good / F = Fair / P = Poor / D = Dark colours only / U = Unsuitable

*Compared on the basis of a 50 μ m film thickness.

*** Variable response, depending on actual composition and heat treatment.

Cast material designation		Sui	itability for anodiz	ing		
BS	Alloy type	Protective	Colour	Bright		
LM 0	Al 99.5	Е	Е	Е		
LM 2	Al Si 10 Cu 2 Fe	F	U	U		
LM 4	Al Si 5 Cu 3	G	F (D)	U		
LM 5	Al Mg 5	Е	Е	U		
LM 6	Al Si 12	F	U	U		
LM 9	Al Si 12 Mg	F	U	U		
LM 10	Al Mg 10	Е	F	U		
LM 12	Al Cu 10 Si 2 Mg	F	F	U		
LM 13	Al Si 11 Mg Cu	F	U	U		
LM 16	Al Si 5 Cu 1 Mg	G	F(D)	U		
LM 18	Al Si 5	G	F (D)	U		
LM 20	Al Si 12 Cu Fe	G	F (D)	U		
LM 21	Al Si 6 Cu 4 Zn	F	U	U		
LM 22	Al Si 5 Cu 3 Mn	G	F	U		
LM 24	Al Si 8 Cu 3 Fe	F	F (D)	U		
LM 25	Al Si 7 Mg	G	F (D)	U		
LM 26	Al Si 9 Cu 3 Mg	F	U	U		
LM 27	Al Si 7 Cu 2	G	F (D)	U		
LM 28	Al Si 19 Cu Mg Ni	U	U	U		
LM 29	Al Si 23 Cu Mg Ni	U	U	U		
LM 30	Al Si 17 Cu 4 Mg	U	U	U		
E = Ex	E = Excellent $G = Good$ $F = Fair$ $P = Poor$ $U = Unsuitable$ $D = Dark$ colours only					

TABLE 2 - ANODIZING CHARACTERISTICS OF CAST ALUMINIUM

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others Each	Total
1080A	0.15	0.15	0.03	0.02	0.02		0.06	0.02	0.02	
5005	0.30	0.7	0.20	0.20	0.5-1.1	0.10	0.25		0.05	0.15
5252	0.08	0.10	0.10	0.10	2.2-2.8		0.05		0.03	0.10
5657	0.08	0.10	0.10	0.03	0.6-1.0		0.05		0.02	0.05
6463	0.2-0.6	0.15	0.20	0.05	0.45-0.9		0.05		0.05	0.15

TABLE 3 - SPECIAL BRIGHT TRIM MATERIALS

Factors Influencing the Choice of Anodizing Process

The properties of anodized aluminium depend on a combination of the following factors:

(a) The aluminium alloy.

(b) Pre-treatment processes.

(c) The anodizing process.

(d) Post-anodizing processes

A very wide range of chemical solution have been used or proposed as anodizing electrolyte, such as sulphuric, oxalic, chromic, and phosphoric acids.

Sulphuric Acid

On all alloys except those containing insoluble, constituents anodising in sulphuric acid produces semi-transparent colourless films in thickness up to about 35 μ m. When properly processed and sealed these coatings are suitable for both decorative and corrosion-resistant applications. The appearance of the coatings is considerable influenced by the original surface finish of the aluminium.

The so-called "bright anodising" is achieved by selection alloys based on high-purity (99.7% +) aluminium or alloys based on it, followed by a brightening process and then anodising in sulphuric acid.

At low temperatures, e.g. -5° C to 5° C, the sulphuric acid process gives very hard coatings (known as "hard anodising") and are widely employed in the engineering industry.

The sulphuric acid electrolyte can also be modified to produce films that will withstand a certain amount of forming without disrupting the film. This type of process is used for the anodising (and colouring if required) of continuous strip.

Oxalic Acid

Solution of this acid tend to produce translucent hard yellowish films that have been used for architectural applications. The abrasion resistance is almost doubler that of a conventional sulphuric acid-process coating. This process is one of the earliest integral colour processes to achieve universal recognition.

Chromic Acid

This acid was used in the first commercial anodising process invented in 1923 by Bengough and Stuart. It produces thin films that are usually opaque grey in colour. It is still widely specified for the treatment of aircraft components for four reason in particular:

- 1. It is a good base for subsequent painting.
- 2. The minimum amount of aluminium is converted during the process, thus reducing any loss of metal thickness on thin stressed sheet components.
- 3. The lost in fatigue resistance is lower than in the case of sulphuric acid.
- 4. If chromic acid becomes trapped in, for example, riveted or over-lapping joints it is less likely than sulphuric acid to cause corrosion.

Chromic acid anodising is also used for crack detection, e.g. in forgings. The orange/red electrolyte oozes from cracks after anodising and colours than dry coating.

Phosphoric Acid

The anodic films produced in phosphoric acid have larger pore diameters than in conventional sulphuric films. This greater diameter provides a better conducting path and it is for this reason that phosphoric acid films have been used as one of the methods for pre-treating aluminium prior to electroplating. During the latter process the anodised aluminium is used as the cathode and plated, for example, with nickel. The phosphoric acid process is rarely used as a finish in its own right due to the existence of more convenient processes.

A closely defined phosphoric acid-anodizing process has recently been adopted to prepare aluminium for adhesive bonding for aircraft components.

Solution Agitation in Anodizing

Stainless steel exchangers have replaced cooling coils, aluminium cathodes have replaced lead plate and eductor systems have been installed to provide solution agitation.

The process of anodising generates considerable heat which if not carried away from the barrier layer of the work causes poor quality coating. If the temperature of the electrolyte can be maintained at 21° C (70°F) for Type II of or 0°C (32°F) for Type III anodize, the formation of the oxide will be dense and uniform. Excessive heat build-up around parts can result in soft, powdery coating of particularly hardcoat anodizing, catastrophic failure or "burning" of the

work. Agitation, therefore, is required so that a constant temperature is maintained within the bath (Brace & Sheasby).

Agitation can be accomplished in a number of ways. We used electric mixers with 7.5–12.7 cm (3"-5") diameter propeller bladed to move the electrolyte in our small tanks. The three primary advantages of this system were ease of installation, ease of maintenance and low cost. While these electric mixers were effective in the small tanks, we did not consider this method when we upgraded to the 1,000 gallons tanks because they provided limited volume movement.

Air agitation is probably the most common method for agitating anodize tanks. This system use high volumen, low pressure blowers which force air through porous plastic pipes or pipes with small holes drilled at closely spaced intervals. Advantages of this system include low operating costs and good heat distribution, even in large tanks. Drawbacks to air agitation include the potential for oil from the blower to be passed into the bath, the noise of the blower, piping requirements from the blower to the bath, possible space constraints for the blower and the potential for the air bubbles to insulate the parts from the electrolyte.

It can be said that the use of very small air bubbles, as compared to conventional air agitation, will improve oxide thickness, uniformity, brightness and smoothness. Despite the effectiveness of air, this work identifies an additional drawback from air. With micro-explosive air agitation, a higher voltage was required, by comparison with that for conventional air agitation. If higher voltages are required, it seem clear that higher operating costs, and potentially larger power supplies will be required when air is used.

Ultrasonic agitation has been used in electroplating. Ultrasonics produces a uniform agitation throughout the bath, compared with mechanical stirring, which causes a laminar flow close to the electrode surface. It is possible that this methods might be effective for anodizers since our objective is to drive heat off of the barrier layer of the anode and the laminar flow would direct the heat away from the work.

Finally, vibratory agitation has been used in the electroplating of circuit boards. This system, may have potential for anodizers although the turbulent eddy patterns may prove to create zones within the tank where the electrolyte is not effectively moving around the parts.

The premise for solution agitation is that if the electrolyte is moving past the work in sufficient volume and with sufficient force then the heat generated during the anodizing process will be driven off the part. As this heat is dissipated by the electrolyte movement, cool electrolyte replaces the heated solution and the part remains at the optimal temperature.

To accomplish the solution movement, a system of pumps, pipes and eductors are used to move the electrolyte. Eductors are Venturi nozzles through which are pumped a given volume of fluid. The nozzles entrain approximately four times the volume of fluid which is being pumped to provide considerable fluid movement. That is to say, if one gallon of fluid per minute is pushed through the inlet, approximately five gallons of fluid are pushed though the outlet.

There were several challenges in adopting the eductor system, none of which were immediately obvious when doing the initial installation. The first assumption, based on our experience with mechanical mixers was that if the electrolyte was rolling it would wick off the heat. The initial installation consisted of a 0.75-1.5 HP pump and six eductors, three per side, equally spaced along the length of each of the nine foot tanks. This construction resulted in slowly moving electrolyte which seemed effective for the Type II tank but at start-up it was clear that hard-coat anodizing could not be performed without more fluid movement. As a result, we immediately added another 1 HP pump and six more eductor to the Type III tank.

With the system described above, it was produced some parts with smooth, hard, dense coating but each tank had some apparent "death zones" where the electrolyte was not moving sufficiently to dissipate heat. Parts located in the dead zones exhibited a soft, velvety appearance or were burned under higher amperage conditions. Therefore, it was very important to quickly solve the problem of the dead zones.

Experiment

Since Type III anodizing is performed with higher current density that type II, it was assumed that solving the agitations problem in the Type III tank would solve the problem for both tanks. We determined that we could identify the dead zones if we could get burning to occur at predicted locations. After identifying the dead zones, we could eliminate them by forcing more fluid movement into these areas.

To identify the dead zones, racks were prepared with four aluminium panels approximately 12.5 x 50.5 cm (5" x 20") bolted to an aluminium spine. Four of these assemblies were placed end-to-end down the center of the tank so that the complete length and depth of the tank was covered. These racks were then anodised to achieve .003"-.005" coating thickness at 20-25 amp/dm². At the end of the run, burning was observed along the top and bottom edges of the racks. Since this could be repeated with the same results each time, it was concluded that there were the needed to "focus" the eductors to more effectively circulate the electrolyte.

Graphical Analysis

Eductors have a conical discharge, the diameter of which enlarges the farther the fluid moves. The rate at which the diameter enlarges depends on the angle of the walls of the eductor. An eductor discharge plume can be described as shown in Figure C.



Figure C

The actual shape of the discharge plume must be determined by reviewing the manufacturer's information which should provide the plume diameter at a known distance.

For the 1.27-0.85 (3/6"-3/9") inlet diameter eductors were used. The supplier of the system indicated that the discharge plume has a diameter of 48.75-57.90 mts (1.6-1.9- feet) at a distance of 243.83-365.75 mts (8-12 feet) from the eductor. While we did not know the force of the discharge, by observation, we determined that a about five feet from the eductor, the force of the moving fluid was almost completely dissipated. With these things in mind, using graphical analysis, it can be determined how to lay out the eductors so that no dead zones result. Figure D shows the tank from the end view.

To prevent inadvertent contact between the anodes (the work) and the cathodes, we installed plastic screen 7,62-12.70 cm (3"-5") off the edges of the tanks. This is significant because the pipes which carry the electrolytic are locates inside the screens instead of in the corners of the tank. Although the tank width (TW) was 101.6-127 cm (40"-50") we had to subtract 7.62-12 cm (3"-5") TW to determine the proper angles to focus the eductors.



Figure D

A radius can be described from the edge of the pipe (where the eductor will be locates) to the waterline. By drawing an arc of the circle with this radius, and knowing the diameter (PD) of the discharge plume at this distance from the eductor, we can describe the effective area covered by the eductor. Let one edge of this discharge plume intersect the tank at the waterline and draw a chord with length PD to intersect with the arc. The triangular area defined is the effective area covered by the eductor.

The angle at which this eductor should be focused (A) can be determined as follows. Bisect PD and draw a line from this point to the eductor. This line defines de centerline of the discharge plume. Continue the centerline to the point where it crosses a line extended upward from the top of the tank. The distance H is determined by measuring the distance from this intersection to the center of the pipe. Angle A is then calculated as follows:

1) $A = \tan^{-1} H_1/TW$

In our system the pipes are located 7.62-12 cm (3"-5") off the tank wall so we has to adjust the above equation to be:

2) $A = tan^{-1} H_1 [(TW-7.62-12 cm)]$

As Figure D shows, more that one eductor is required to provides circulation throughout the tank. Figure E shows that four eductors, two to each side, with different focus angles will almost cover the tank zones although there are four small dead zones which must be addressed.



Figure E

To determine the focus angles of educto B, a similar procedure to that describe above is followed. The coverage area of this eductors determined by allowing the top edge of the discharge plume to pass through a point at the waterline of the tank and drawing a chord of length PD from that point, downward, to intersect with the arc of the circle. Again, bisecting this chord and drawing de centreline of the plume, defines a focus angle B. The point at which the centreline of this eductor crosses the edge of the tank has a distance from the bottom of the tank, which is equal to H_2 . Therefore, angle B is calculated as follows:

3) 3) $B = tan^{-1} H_2/TW$

Again, adjusting for our pipe location:

4) $B = tan^{-1} H_2 / H_1[(TW-7.62-12 cm)]$

It can be shown by the same technique that is would require 4-6 eductors per side to completely eliminate the dead zones. Since eductors must be located at defined intervals throughout the tank, with four/six eductors per location, a prohibitively large number of eductors would be required. With this in mind, mounting eductors on the end of the tanks was considered.

Figure F shows the side view of the tank with eductors focused into the tank on angles C and D. The same procedures for determining the location of the eductors can be followed for the eductors mounted on the end of the tank as for those located on the side. Draw the arc of a circle with a radius equal to the distance from the pipe to the waterline. Determine the diameter of the discharge plume at this distance, see Figure C, and draw the chords of length PD. Bisect the chords and draw the centerlines of the plumes to define focus angles C and D. Extend the line defining the end of the tank until it intersects with the centreline of the eductor with focus angle C and calculate the angle as follows:

5) $C = \tan_1 H_3/TL$, where TL is defined as the tanks length.

No adjustment was required for the end mounted eductors because there were no cathode screens located on the end of the tanks.

Likewise, determine where the centerline of the discharge plume of the eductor with focus angle D crosses the end of the tank and calculate angle D as:

6) $D = \tan^{-1} H_4/TL$

Figure F shows that the plumes for the eductors mounted on the end of the tanks cross through the dead zones left by the side mounted eductors so no area of the tank is left static.



Figure F

In order to complete the layout of the eductors, it is necessary to consider the tank from the top view. Figure G shows that the eductors are not mounted directly opposite each other. This

was done to prevent the plumes from hitting each other and cancelling each other out. Each side mounted eductor is staggered by a distance equal to 1/4-1/2 PD. Similarly, end mounted eductors with the same focus angle are staggered by a distance equal to 1/4-1/2 PD.



Figure G also shows the relationships of the discharge plumes after being staggered. The side mounted eductors evidence conical plumes which do not intersect because the diameter of the plume is equal to the spacing between the eductors. While the plumes from the end mounted eductors would seem to interfere with each other, we found that the force of each plume was dissipated before hitting the mid-point of the tank. In fact, further work in the plant led to placement of two additional pipes at the mid point of the Type III tank. These pipes were oriented perpendicular to the length of the tank, as are the pipes for the end mounted eductors, and the eductors mounted in these pipes were focused from the mid-point back toward the ends of the tank. The same graphical procedures as described above were used to determine their placement.

Piping Requirements

Although pumps are sized based on the number of eductors to be driven, we found that the temperature of the electrolyte had an effect. Manufacturer's recommendations for the eductors were used were 1 HP for each 6 eductors being driven by the pump. This proved to be adequate for the Type II tank, with an electrolyte temperature of 20-25°C, where a 1.5-2 HP pump drives 10-15 eductors. The temperature for the Type III electrolyte is 0-5°C and, by trial and error, we determined that 4-6 HP was required for 20-30 eductors. For both tanks, the centrifugal pump are mounted over the side with the pump inlets and discharge inboard as shown in Figure G.

Construction

With the plans drawn, construction on this system is relatively simple. 2.5-1.25 cm (1-1/2") diameter CPVC pipe was selected for use with 1.90- 0.95 cm (3/4-3/8") inlet eductors. The pipe was drilled and tapped for the eductors and all connections were threaded. Tees were used to split the circulation pipes so that an equal number of eductors were located on each side of the tee and the ends of each leg were capped. Threaded unions connect the distribution pipes to the pumps to facilitate maintenance.

High Current Density Anodizing

Perhaps the most Effective measure of the cooling and agitation system is hardcoating with high current density. A computer system controls the pulsing current and the current density allows production Type III anodizing at 30-50 amp/dm² and Type II anodizing at 18-24 amp/dm². Development hardcoat applications have ranged as high as 200-250 amp/dm². These higher current densities speed up the anodizing process, improving throughput, but there is more heat generated during the process which must be driven off of the parts.

Military aluminium standard, Mil-A-8625, specifies that hardcoat anodised panels must be abraded by the Taber Test and have a wear index of 1,2-1.8 mg/1000 cycles. We characteristically performed hard coat anodizing at 18-26 amp/dm² in our old system with an average wear index of about 1.0-1.5 mg/1000 cycles. In the new system, hardcoating at 30-50 amp/dm², an average wear index of 0.8-1.5 mg/1000 cycles has been obtained. It is evident that the agitation system is working properly since heat adversely affects coating hardness.

Agitation of Aluminium Anodizing Bath

Agitation of aluminium anodizing bath is not only the most important factor in making the bath temperature uniform but also a factor having great effects on film characteristics. The special air agitation method using a diffusional air pipe in an anodizing bath, is called micro explosive method. In the micro explosive air agitation method, the surface of a product is continuously surrounded by fine bubbles, and Joule Heat generating from the barrier layer during anodizing is quickly eliminated by diffusion. So by applying micro explosive air agitation, ordinary temperature high speed (hard) anodizing is enabled and other various effects can be obtained. Since fine bubbles are generated in the entire tank and agitate the solution, the uniformity of the bath temperature is improved, the products will stable quality film can be obtained.

In the present study, in order to compare effects of micro explosive air agitation with those of ordinary agitation, experiments were performed from various view-points of anodizing, and properties of obtained films were evaluated.

Experiments

Experiment tank

The electrolyte tank shown in Figure G was used for comparison with the ordinary air agitation method. The diffusional air pipe used was made of sintered ceramic prepared by burning Aluminium-type artificial abrasive at a high temperature.



The surface structure of the pipe is as shown in Fig. H. The pore size ranged from about 30 to 50 μ m. the piping at each plant, vertical or horizontal piping, is determined according to the shape of the tank. The air pipe can provide bubbles uniformly up to about 1.5 M. When air is sent from both ends, 3 M is the standard length to the pipe.

Aluminium Test

The basis electrolytic bath was composed of 180-200 gr/l of sulphuric acid and 5-6.2 gr/l of dissolved aluminium ($A^{\beta+}$). High concentration baths (special baths) were used for copper-aluminium alloy and high silicon-aluminium alloy.

Electrolysis was performed by the direct current process at a bath temperature of $0-30^{\circ}$ C and current density of 1-6 A/dm². Electrolysis process without agitation, with ordinary air agitation (air volume: 20-80 l/min/m) were compare.

Examination Items

- Bath voltage
- Colour of film, including brightness
- Film thickness distribution
- Limit of film burning
- Surface roughness
- Hardness of film
- Dye affinity of film
- Sealing effects of film and finishing

Results

Bath Voltage

The voltage of ordinary electrolysis (20-25°C, 1-3 Amp/dm²) with agitation is shown in Table 1. The bath voltage was highest in the micro explosive air agitation method. Followed by the ordinary air agitation method an no agitation method. The voltage hardly varied with the change in the intensity of micro explosive air agitation. The reasons for the high voltage in the micro explosive air agitation method are assumed to be that fine bubbles dispersed in the bath cover flow of electric current and the temperature around the film decreased by diffusion of Joule heat. Figure I shows the V-T curve in high speed anodizing by the micro explosive air agitation method. At low temperature, the bath voltage rapidly rose with film thickening. As the temperature rose, the slope of the V-T curve became low with film thickening. Joule Heat generated from the barrier layer during anodizing becomes small as the voltage decreases. The bath voltage needed to obtain a certain film thickness becomes low as the bath temperature rises. It is clear, therefore, that high speed anodizing are 20-30°C with micro explosive air agitation reduces the burden on a freezer and is very economical.



Figure I - Bath Voltage – Anodizing Time (V – T) Curve at Micro Explosive Air Agitation

Colour of Film (Including Brightness)

Table 4 gives the changes in colour of films produced by normal and micro explosive air agitation methods with the change in bath temperature.

Examination by colour difference meter or visual test revealed little difference in colour between films produced by the two methods. However, there was some difference in brightness. The brightness of film before anodizing was more favourably maintained in the micro explosive air agitation method than the ordinary agitation method. The reflectivity of test pieces undergoing chemical brightening was measured before and after anodizing. Obtained results are compared between the two agitation methods in Table 5. The micro explosive air agitation method is suitable for anodizing of copy machine parts requiring reflectivity and decorations requiring brightness.





Film Thickness Distribution

Film thickness distribution was compared between micro explosive and ordinary air agitation methods using the JIS 1050 aluminium nameplate and JIS A 6063 aluminium extrusion plate. Figure J shows the sites of film thickness measurement after anodizing. Conditions of the measurement and results are given in Table 4, 5 and 6.

In case of aluminium nameplate, the average value of film thickness was comparable between the two agitation methods. The standard deviation (uniformity of film thickness) was better (more uniform) in micro explosive air agitation. This difference became more marked with current density elevation. As to film thickness distribution, film was thin at the central parts indicated a B and E, and tended to be thick at the lower portion of both ends indicated as G and I. This tendency was more marked in the ordinary air agitation method that in the micro explosive air agitation method. When aluminium nameplate was hung parallel or vertical to the cathodes, there was a great difference in the standard deviation (uniformity). The arrangement became parallel, and the uniform coating ratio rose. Application of micro explosive air agitation made the uniform coating ratio higher.

Table 6 shows film thickness distribution observed when the aluminium extrusion sheet was vertically hung. The film tended to become thicker at the lower portion that in the upper portion. This tendency became more marked in the ordinary air agitation method with increase of current density. It was revealed that uniformity of film thickness is elevated by micro explosive air agitation, and that this effect was more marked under electrolytic conditions generating a greater amount of Joule Heat. In practical production lines, this uniformity of film thickness brings good practical results in anodizing of precision parts including electronic parts and large materials including electronic piano panels.

Limit of Film Burning

The limit for current density in producing good quality film is $1-3 \text{ amp/dm}^2$ in the ordinary air agitation method. In the micro explosive air agitation method, the current density could be elevated to 5-6 amp/dm². Table 7 shows the relation between air density and film burning in both agitation methods with the limit for current density (to 5-6 amp/dm²) examined using aluminium moulded plate. These results indicate that micro explosive air agitation has a superior burning prevention effect even at the low air intensity. In practical production lines, this agitation method is widely applied to anodizing of copper-aluminium alloys liable to burn and hard anodizing by high current density electrolysis at ordinary temperature.

Surface Roughness

The surface roughness of the (aluminium casting) cylinder cutting part was measured before and after anodizing with the two agitation methods. Results obtained, shown in Figure K, indicate the surface roughness due

to anodizing can be reduced by micro explosive air agitation.

Micro explosive agitation is suitable for anodizing of cutting parts and aluminium diecasting, casting and alloys which are liable to become rough during electrolysis.





Film Hardness

Vicker's Hardness on the cross sections of hard anodised films 20-25°C, 2-6 amp/dm² 60-110 μ m) produced with the two agitation methods is compared in Figs. I and J. In these figures, the biggest rhomboids of diamond indentor trace indicate softer film. In the ordinary air agitation method, the film hardness decreased stepwise from the inner to outer layers of the film (HV 410 \rightarrow HV 260). The hardness was almost constant in films produced with micro explosive air agitation (HV 430-410). In the ordinary air agitation method, it is assumed that since the films layers produced in the early period of electrolysis are gradually dissolved because of generated Joule Heat and becomes coarse, the film becomes softer as it comes close to the surface. It is believed that in the micro explosive air agitation method, the hardness becomes uniform owing to favourable dispersion of Joule Heat. Elevation of surface hardness contributes to improvement of abrasion resistance.

Agitation Method	Air volume (L/min/M)	Bath Voltage (V)
Without Agitation		14.6
Normal Air Agitation	22	15.1
Micro Explosive Air Agitation (Weak)	22	17.0
Micro Explosive Air Agitation (Middle)	44	17.5
Micro Explosive Air Agitation (Strong)	66	17.5

Table 4 – Change of Anodizing Bath Voltage

(Anodizing Condition: 1 A/dm^2 , 25° C, Al 6060)



Figure L – Rough Sketch of Constructions of Films by Both Agitation Methods

Fable 5 – Brightness M	aintenance Ratio at	Both Air Agitation	Methods
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Agitation Method	Anodizing Temperature ([•] C)	Film Thickness (🖿 n)	Absolute Reflectivity (%)
			88.4 - 89.2
	20	12	69
	20	25	70
Normal Air Agitation	22	12	71
Normai Ali Agitation	22	25	70
	28	12	69
	28	25	68
	19	12	72
	19	25	69
Micro Explosive Air	22	12	73
Agitation	22	25	69
	28	12	72
	28	25	69

Current Density: 1.5-3 Amp/dm². Film Thickness Measurement: Permascope EW-09 Reflectivity Measurement: 15°. Measurement Wave of Absolute Reflectivity: 500-600 nm

Agitation Methods	Anodizing Conditions (25°C)	Disposition of Jigging	Average of Thickness at 9 Positions (mm)	Standard Deviation (mm)
Normal	1-3 A/dm ²	Parallel-ward	7.8	0.425
Air	25 min	Vertical-ward	7.5	0.864
Agitation Method	1-3 A/dm ² 15 min	Parallel-ward	8.5	0.755
		Vertical-ward	8.5	1.382
Micro	1-3 A/dm ²	Parallel-ward	7.8	0.244
Explosive Air Agitation Method	25 min	Vertical-ward	7.7	0.395
	1-3 A/dm ²	Parallel-ward	8.7	0.495
	15 min	Vertical-ward	8.7	0.690

Table 6 – Distribution of Film Thickness at Bath Agitation Method on Aluminium Articles (Anodizing Condition: 1.5 A/dm²: 35 min)

Table 7 – Relation Between Current Density & Standard Deviation of Film Thickness
at Both Air Agitation on Aluminium

	Nort	mal Air Agitat	tion	Micro E	xplosive Air A	gitation
	Upper	Middle	Below	Upper	Middle	Below
Specimen 1	15.5	16.8	18.8	16.0	16.7	17.4
Specimen 2	15.4	16.8	18.2	16.1	16.2	16.9
Specimen 3	15.6	16.8	18.0	16.9	17.0	17.4
Specimen 4	15.6	17.0	18.2	16.8	17.2	17.5
Average Thickness	15 - 18 μm			15 - 18 μm		
Standard Deviation	1.004				0.655	

(Unit: µm)

Table 8 – Relation between Current Density & Standard Deviation of Film Thickness at Both Air Agitation Methods and Aluminium Article

Anodizing Condition	Normal Air Agitation (m n)	Micro Explosive Air Agitation (m m)
1.0 A/dm ² (25°C, 45 min)	0.465	0.389
1.5 A/dm ² (25°C, 30 min)	0.879	0.495
2.0 A/dm ² (25°C, 25 min)	1.555	0.666

(Thickness: 15 µm)

Air Volume (L/min/M)	Normal Air Agitation	Micro Explosive Air Agitation
10	Burning & Powdery Bloom at Lower Parts	
20	Slightly Burning at Lower Parts	Burning at Upper Parts
30	Slightly Burning at Lower Parts	No formation of Burning (Good Condition)
40	Slightly Burning at Lower Parts	No formation of Burning (Good Condition)
60		No formation of Burning (Good Condition)
80		No formation of Burning (Good Condition)

 Table 9 – Influence of Air Volume of Air Agitation to Burning of Film

(Anodizing conditions: 20°C, 5 A/dm², 20 mm)

Conclusion

- 1. Solution agitations is a viable alternative for both Type II and Type III anodizing. Using centrifugal pumps CPVC pipes and eductors provides a system which is easy to construct and maintain.
- 2. In addition, Taber Test results have shown that solution agitation, is sufficient for use in high current density applications. The combination of high current density and good heat dissipation can be used to speed up production while improving the wear index of the parts.
- 3. Micro explosive air agitation method diminished distribution and improved the uniformity of film thickness distribution and improved the uniformity of film thickness. This property id advantageous in anodizing of precision parts and products of large size and complicated shape.
- 4. No significant difference in colour were observed between the two agitation methods. However, the micro explosive air agitation method had a better brightness retaining effect that the conventional method. This property is suitable for anodizing of functional parts and decorations.
- 5. The micro explosive air agitation method had excellent film burning preventing effects. Therefore, high speed and high temperature (20-40°C) anodizing methods are possible. This property is effective for speeding up anodizing of black coated products requiring thick coating.
- 6. Surface roughness was lower in the micro explosive air agitation method than in the ordinary agitation method. This property is suitable for cutting parts (cylinder, etc.) in which the surface roughness is important, and aluminium die-casting alloys and casting which are liable to become rough.
- 7. The micro explosive air agitation method could improve the quality of film surface in hard anodizing (the decrease in film hardness was slight).
- 8. The micro explosive air agitation method provided films with favourable sealing effects. Appearance of powdering and blooming during sealing was depressed and finishing was improved.

9. References

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