HEA - HIGH EFFICIENCY ANODIZING
A Unique & Progressive System Designed to Produce High-Speed, High-Throughput Anodizing

Authored By Dr. Enzo Strazzi and Silvia Bellei
Research and Development Laboratory
Italtecno S.r.l. Modena, Italy

Edited and Presented by
Dennis G. Duncan, Division Manager
Aluminum Finishing Division - North America
Chemetall Oakite

Chemetall Oakite
Member of the Chemetall GmbH Group
Exclusive Licensee of
Italtecno S.r.l. Modena, Italy

The Authors investigated the possibility of obtaining high-speed formation of the anodic oxide layer while maintaining the quality required by international standards. This research was approached from different directions:

1. Chemical parameters (composition of the solution, influence of the various additives on the layer of oxide);
2. Physical parameters (agitation method and temperature of the solution, current density);
3. Machines (current rectifiers, equipment to automatically gauge the thickness of the oxide as it forms) used to simply obtain the required characteristics consistently.

The characteristics of the layers of anodic oxide were checked as the current density varied from a low of 10 to 60 A/Ft^2. Their coloring intensity was also verified.

Numerous graphs and tables showing the results of the experiments are given.

Thirty-two (32) bibliographic references are also indicated.

For More Information Contact:

Dennis G. Duncan
Division Manager, Aluminum Finishing Division-North America
Chemetall Oakite
50 Valley Road, Berkeley Heights, NJ 07922

Office : (800)526-4473 x 2428   FAX : (208)330-5108

1. Foreword

One of the dreams of anodizers has always been that of producing the anodic oxide layer within the shortest possible time (obviously while safeguarding quality). The anodizing quality control authorities have established the following parameters for anodizing (1):

Sulfuric Acid	less than 200 g/l
Dissolved Aluminum	less than 20 g/l
Temperature	lower than 68º F
Current Density	between 14-18 A/Ft^2

The above listed parameter margins are fairly narrow and do not leave much space for significant innovations. It is not the Author's task to discuss the validity of the above mentioned values. The spirit with which they were established was undoubtedly that of defining ranges within which the quality of anodized aluminium was certain and well identified.

In practice, researchers have often worked beyond these parameters with perfectly acceptable quality results when opposite effects (e.g. treatment time and anodizing temperature, or current density and the coloring intensity of the material) were balanced in relation to each other.

1.1 The Effects of the Anodizing Parameters on the Properties of the Anodic Layer

The following are the most important parameters that influence the layer:

- Concentration of sulfuric acid in the electrolyte
- Temperature of the electrolyte
- Applied voltage and/or current density resulting from the previous parameters
- Efficiency of the agitating action with air and cooling of the electrolyte

All these parameters contribute toward the determination of another important factor, i.e. the cost of energy. Electric current is paid for in *Kilowatt-hours (kWh)* and the peak power draw values and times of use often establish its price:

Volts (V) x *Amperes (A)* x *time (h) = Wh*

A high current density or a higher voltage rating involves a higher energy cost. In order to maintain the same current density, a lower voltage rating requires a higher concentration of acid, a higher temperature or a longer processing time to obtain the same thickness of oxide. Longer dipping times and/or higher temperatures actually produce softer layers.

1.2 Sulfuric Acid Concentration

Despite the fact that maximum conductivity is obtained with about 350 g/l of sulfuric acid, the acid concentration is usually kept between 150 and 250 g/l, since higher values tend to give softer layers. The weight of the oxide layer and, thus, the thickness, decreases as the acid concentration increases as does the ability to withstand abrasion, indicating that a softer layer forms.

1.3 Effect of the Temperature of the Electrolyte

The effect of the temperature can be briefly outlined in the following way:

High Temperatures Produce . . .

a) Layers with a lower apparent density (specific weight), and are softer but more glossy,
b) Greater difficulty in sealing the pores because the outer part of the layer tends to become soft and crumbly,
a) Layers that are more easily colored; however, with colors that are more difficult to reproduce, especially if the adsorption dyeing method is used.
b) Faster colorings (of a more pinkish shade) if the electrolytic method is used with tin, nickel or cobalt salts.

Lower Temperatures Produce . . .

a) Harder layers with better resistance to abrasion,
b) Harder layers that require higher voltage ratings to reach the same current density.

1.4 The Effect of Voltage

The applied voltage influences the porosity of the layer since lower voltage ratings give smaller, but more numerous pores, while higher voltage ratings give larger, but less pores.

1.5 Effect of the Current Density

If the current density remains constant, the thickness of the produced layer will be directly proportional to the anodizing time.

The current density is maintained by a progressive increase in voltage, able to compensate for the increase in resistance caused by an increase in the anodic layer. The effects of current density will now be described.

A Low Current Density (e.g. 10 A/Ft^2) Gives . . .

a) Greater gloss,
b) But at a low anodizing

A High Current Density . . .

b) Leads to rapid layer formation, but with a greater risk of soft layers and burning,
c) Produces a greater amount of heat at the layer-electrolyte interface and therefore requires an adequate agitation or mixing system for the electrolyte,
d) Improves the resistance to abrasion with adequate agitation and cooling.

1.6 Agitation

Agitation is mainly carried out to eliminate the heat produced on the surface of the layer during the electrochemical process. Practical experience has shown that the best result is obtained by blowing in air through special diffusers that produce bubbles of a very small diameter (better if less than 2 mm). Simple agitation is obviously not enough to maintain the solution at the correct temperature. It is therefore also necessary to install a cooling system with a heat exchanger, the power of which, calculated according to *Euras Qualanod* indications (1), will be:

0.86 x *Ampere* x *(Volts + 3) = Kilocalories hour*

1.7 A Few Rudiments of Physics

The electrochemical basis for the production of anodic oxide is *Faraday's* law, according to which the quantity of metal deposited on the cathode or dissolved by a soluble anode is proportional to the total electric charge passed. In other words: for the same quantity of electricity, the quantity of metal deposited on the cathode or dissolved by a soluble anode is proportional to its electrochemical equivalent.

In the case of aluminum, acting as an anode, the quantity of aluminum transformed into aluminum oxide is proportional to the total electric charges passed. In other words, *1 equivalent gram* of aluminum metal is converted into *1 equivalent gram* of aluminum oxide by *96.501 Coulombs* of electricity (i.e. *1 Faraday*) allowed to pass through the electrolyte.

Remember that the electric charge unit known as *Coulomb*, corresponds to *1 Ampere* (current intensity measurement) for 1 second. It will therefore be evident that, at a constant current density, the thickness of the oxide layer will be proportional to the anodizing time and that in any case, the oxide thickness depends on the number of electric charges passed (*Coulomb*), which can be expressed as *0.1076 Amperes/Ft^2* x *time*.

In short:

- The thickness of the layer is proportional to the *Coulombs* passed, i.e. to current density by time.
- The thickness of the layer does *not* depend on the voltage.
- In industrial conditions, 506 *Coulombs/Ft^2* are needed to produce *25 microns (1.0 mil)* on alloys 1000, 1100, 5005, 5052 and 6063, approximately *592 Coulombs/Ft^2* for alloys such as 6061, 6082 and over 678 *Coulombs/Ft^2* for alloys with a high concentration of copper.
- The number of *Coulombs* is obviously highly influenced by the condition of the electrolyte, particularly temperature and acid concentration, i.e. the parameters that can influence the speed with which the layer of oxide is dissolved.

2. Description Of The Equipment Used For The Experimental Part

This work is the result of lengthy experimentation with the pilot anodizing plant of Italtecno, consisting of a total of 16 tanks measuring 700x400x500(h) and amounting to a volume of about 37 gallons.

The cleaning and chemical etching, sealing by low temperature impregnation and subsequent hot treatments were kept at the below listed operating temperatures by thermostats.

The material was washed under running mains water, the flow rate being sufficient to ensure an hourly change for each individual rinse, while the rinse prior to the cold sealing process was in demineralized water.

The anodizing tank was equipped with aluminum electrodes that almost entirely covered the side surface of the tank itself, which was also equipped with a cooling and agitating system using filtered compressed air.

The solution was cooled by means of a heat exchanger, while an efficient pump kept the solution itself continuously on the move. The inlet and outlet pipe arrangement allowed all the solution to be subjected to a convection movement.

This homogenized the electrolyte in order to keep the temperature and heat dissipation owing to the *Joule* effect, at uniform levels. Tests had showed (and similarly to what occurs in certain industrial systems) that agitation obtained by means of a pump was sufficient to guarantee the correct quality of the anodic layer without the further need for agitation with air if the anodizing parameters were kept within the standard ranges.

A chilling system and exchanger kept the temperature of the oxide bath +/- 1.0º F in relation to the desired value, which was indicated by a digital thermometer installed on the control panel of the apparatus.

A high efficiency tin salt based solution was used for the coloring tests. Tanks with nickel salt (for bronze and black colors) and potassium permanganate (for gold coloring) based solutions were, however, available. In relation to our research, the behaviour of these baths was in line with that containing tin salts.

The same power supplier* was connected in parallel to both tanks for the anodizing and coloring processes. It supplies:

a) Pulsating direct current,
b) Conventional alternate current,
c) Alternate current at variable and independent frequencies for the negative and positive phase.

The machine was equipped with a sophisticated computer through which it was possible to define and enter the operating parameters and, if required, record their graphs on the PLC during the execution phase.

3. Description Of The Anodizing Process And Composition Of The Treatment Solutions

The samples were subjected to an anodizing procedure consisting of the following phases.

*3.1 **Cleaning** in the following conditions:*

Cleaner Concentration	5% bv
Temperature	113º F
Immersion time	10 minutes

*3.2 **Etching**, in the following conditions:*

Free caustic	11.7% bv
Dissolved aluminum	90 g/l
Additive Concentration	1.3% bv
Temperature	131 +/- 4º F
Immersion time	10 minutes

*3.3 **Rinsing** in running water*

*3.4 **Neutralizing**, in the following conditions:*

Sulfuric acid	120 g/l
Additive Concentration	3% bv
Temperature	ambient
Immersion time	2 minutes

*3.5 **Rinsing** in running water*

*Tecnocolor, manufactured by, Elca, available through Italtecno S.r.l., Modena, Italy

*3.6 **Anodizing**, in the following conditions:*

Sulfuric acid	180 g/l
Dissolved aluminum	5 g/l
Additive as indicated for the individual tests	
Temperature as indicated for the individual tests	
Current density as indicated for the individual tests	
Thickness of the anodic oxide layer	20 +/- 1 micron (0.8+/- 0.04 mil)

*3.7 **Rinsing** in running water*

*3.8 **Electrocoloring** in the following conditions:*

Tin sulfate	17.5 g/l
Total acidity, as sulphuric acid	22 g/l
Stabilizer Concentration	50 g/l
Temperature	ambient (72º F)
Counter-electrodes	tin

Coloring programs as indicated for the individual tests

*3.9 **Rinsing** in running water*

*3.10 **Rinsing** in demineralized water*

*3.11 **Sealing** by impregnation in the following solution:*

Seal Concentration	1.5 % bv
Temperature	82 +/- 2º F
Immersion time	1 min./micron (20 min.)

*3.12 **Rinsing** in running water*

*3.13 **Hot Immersion**, in the following conditions:*

Demineralized water	
Temperature	140 +/- 2º F
Immersion time	5 min

*3.14 **Drying***

The test pieces were allowed to dry in the air without further treatments. None of the pieces (either coloured or natural) showed signs of iridescence or sealing bloom and could therefore be used for the following tests without further treatments.

4. Aluminum Materials For The Tests

Unless otherwise indicated, samples made of aluminum alloy 1050 - H 18 measuring 3"x 4" and 0.6" thick, each with an area of 24.84in^{2}, were used for the tests. The plates were attached in pairs on S-shaped aluminium hooks so that contact was guaranteed by the spring effect of the aluminum rod (diameter 6 mm). This type of attachment left no marks on the visible surfaces of the samples. The immersed area of each individual attachment, including the hook, was 3.3 dm^{2}. 6 attachments each with 2 plates were used for each test, amounting to a total 19.8 dm^{2}.

5. Description Of The Experimental Part

Considering the entity of the experiments, the Authors attempted to follow a logical and functional course in order to achieve their target: *demonstrate that it was possible to obtain anodic oxide of a similar quality to that produced with conventional systems but much faster and at lower running costs*. They therefore defined the following schedule:

a) Verification of the voltage and current density trend,
b) Anodizing speed as current density varies,
c) Quality of the oxide layer as current density and temperature vary,
d) Coloring intensity of the oxide layer produced in the above mentioned conditions.

5.1 Voltage Trend as the Temperature and Current Density Vary

Strips of aluminium alloy 6063 measuring 23.6" x 2.4"x 0.08' were used for this test, during which they were immersed to a depth of 17.3", indicated by a mark made on the test pieces themselves. The immersed area for each test piece was 84.5 in^{2}.

To conduct the tests with the same current intensity, 4 strips were used for tests with 10, 15, and 20 A/Ft^2 current densities, 2 strips with 30 and 40 A/Ft^2 current densities, and one single strip with a current density of 60 A/ft^2. Strips were preferred for this test since they offered a larger area of contact between the test piece carrier bar (accurately cleaned) and the samples themselves.

The temperature was reached by means of a ceramic heating plug and a heat exchanger, if it was necessary to cool. The computer that handled the power supplier was given an indication as to the real immersed surface and the desired current density, which was reached within a ramp time of 30 seconds (value normally used in industry).

The effectively reached voltage was read by means of a digital voltmeter, the prods of which were set on the bar carrying the test pieces and on the cathode of the anodizing tank.
The data are given in *Table 1* and *Graph 1* and show the significant influence exercised by the temperature required in order to reach a certain current density.

5.2 Determination of Anodizing Speed as the Current Density Varies

Operating with a constant current rate, the speed with which the layer of oxide forms does not depend on the temperature of the electrolyte if this is not able to excessively influence the speed with which the layer dissolves. The temperature of the electrolyte influences (cfr. ß 1.3) the voltage required to reach a certain current density, but the layer of oxide is formed by the current that passes (*Coulomb sec. = Ampere*). A temperature was therefore defined (66º F) and the heat exchanger, the acid circulation pump and the agitation/aeration system of the solution were therefore operated for this test.

The process computer was given the following indications:

a) Immersed surface,
b) Current density to apply,
c) Required thickness: 20 microns (0.8 mil).

The total processing time was recorded for each test. The obtained thickness was systematically 20 microns / 0.8 mil (with the tolerance due to the measuring instrument) because the machine counted in *Amperes-hour*, thus the gauged times could be considered correct.

The experimental data given in *Table 2* and represented by *Graphs 2* indicate a direct proportionality between the time taken and the current density, i.e. the greater number of *Amperes* that pass per unit of area, the quicker the layer of oxide forms.

The values given in the table can be used to determine the ratio between *Amperes/hour*, square feet of area and microns (mils) of formed oxide thickness. For example, 44 minutes are required to produce 20 microns (0.8 mil) when operating at 15 A/Ft^2 thus, to produce 1 micron on 1.00 m^2 (10.76 Ft^2) :

(15) (44/60) (100/20) = 5.5 x *Amperes-hour (Ah)*

This value has been fully experimented in our laboratory and is currently used as a reference when programing the device** installed on the current rectifiers which acts as a *thickness pre-setter.* The device stops anodizing once the pre-set value in microns has been reached and gives a correct indication of the *electrolytic* area that is anodized. Determination of the *electrolytic* area, which often does not coincide with the *visible* area, is of great use in automatic and computerized systems or when special colorings are produced

Despite the fact that the results of *Table 2* were highly encouraging, the authors wished to verify the quality trend of the anodic oxide layer as temperature varied.

This was the only parameter that could significantly influence the cost of the process, as the required voltage varied to reach a given current density.

Table 3 gives the consumption in *Kilowatts-hour* per square foot of treated aluminum as the current density and temperature varied.

**APC, manufactured by Elca, available through Italtecno S.r.l., Modena, Italy.

The calculation was made in the following way by means of the data in *Table 1* and *Table 2*:

$$KWh\ /Ft^2 = V \times (A/dm^2) \times (.00929) \times (T/60)$$

where V is the voltage,
A/dm^2 is the current density (the initial tests were performed in A/dm^2),
.00929 is the factor of conversion from dm^2 *to* Ft^2,
T is the time in minutes,
60 is the conversion factor to convert minutes into hours.

Calculation example:

at 66º F and 1.5 A/dm^2 (or $15A/Ft^2$), it is necessary to operate at 18 Volts for 44 minutes to obtain 20 microns thus, the necessary *Ah* are:

$$18.0 \times 1.5 \times (.00929) \times (44/60) = 0.184\ KWh\ /Ft^2$$

The data in *Table 3* indicates that the temperature increase is usually great enough to completely balance the higher consumption in KWh that are produced by the increase in current density (lowering the voltage). Secondly, the greater productivity of the system is significantly able to reduce the cost per Ft^2 of the finished material.

Production costs overall are lowered when one considers the lower incidence of plant depreciation, tank heating, and labor costs, especially when the average thickness of the oxide layer is 15-20 microns, and the workers on the anodizing line tend to have a fair amount of down times.

5.3 Quality of the Oxide Layer as the Current Density Varies

At this point, the preliminary problem posed was that of evaluating the quality of the oxide layer in a simple and discriminating way. Among the various methods, we tried to use the one that in our opinion represented the oxide situation as a whole in the best possible way, not just the characteristics of the outermost parts of the layer. Abrasion tests were not, therefore, considered indicative. We therefore used the apparent density test (specific weight) and the weight loss test. The reason was due to the following considerations:

a) The specific weight test (more correctly known as apparent density since one is not dealing with a compact and homogeneous structure, but a porous mass that when measured, could still contain a certain quantity of air and humidity) was able to give a global indication about the characteristics of the layer;

b) An anomalous oxide layer structure would certainly influence pore-sealing efficiency. The weight loss test in a phospho-chromic solution in compliance with the following standards, *ASTM B-680* and *ISO 3210,* standards that are normally used to check sealing quality, would give a good indication about the characteristics of the anodic oxide layer.

The two tests will now be explained in detail.

5.3.1. Apparent Density of the Oxide Layer

The test was based on the studies of *Elze* (*27)* and the data of *Kissin*, *Deal* and *Paulsen* on various aluminium alloys in a 165 g/l sulphuric acid solution at 12.9 A/Ft^2 at temperatures of 68 and 77º F. The current standards of the *American Aluminum Association* established *2.32* g/cm^3 as the minimum apparent density for *Class 1* layers (18 microns / 0.7 mils), i.e. 4.18 mg/cm^2 as the minimum weight of the layer (2.32 x 18 = 4.18).

Accurate investigation into the apparent density of oxide layers was conducted by *Lenz* (*29*) on aluminium 99:9 and on *Reflectal* (an alloy with 0.5% of magnesium) anodized in 250 g/l of sulfuric acid at 63-65º F, sealed for 20 min. in steam. *Lenz* observed that apparent density decreases from 3.1 g/cm^3 for 5 microns (0.2 mils) to 2.7 g/cm^3 for 20 microns (0.8 mils).

It is true that this type of measurement, preferably made on unsealed materials to avoid the influence of the sealing quality (which depends on the characteristics of the layer caused by the operating conditions), leads to slight measurement error.

The errors are due to the difficulty in checking the thickness of the oxide layer, and its effective uniformity with sufficient accuracy. In the case of our tests, an excessive variation in the layer was limited by the computerized system used to determine the layer itself during the anodizing process.

The layer thickness was determined by the induced current method (*Fischer Permascope*) able to calculate the arithmetical average of the measurements gauged on the same test piece. All the measurements were made on perfectly dry test pieces and the etching time and treatment conditions were checked with the utmost care in relation to these samples in order to prevent different roughness values, due to a different type of chemical attack, from influencing the thickness measurement.

The tested samples were treated in the conventional way as indicated above and after the anodizing treatment. They were very thoroughly washed, first under running mains water and then for 2 minutes in demineralized water at 158º F to speed up the drying process. The samples were then allowed to dry in the air and, after the thickness of the anodic oxide layer had been measured (*s*), they were weighed (*P1*) and immersed in a phospho-chromic solution (given below) in order to dissolve the oxide layer without affecting the aluminum.

The solution was the same used to gravimetrically determine the oxide thickness. 2 samples were used for each individual test and the results in the tables are the arithmetical average of the measured values. Solution used to dissolve the oxide layer:

Chromic acid	20 g/l
Phosphoric acid at 85%	35 ml/l
Temperature	167º F
Immersion time	30 minutes

After thorough washing, first in mains water and then in demineralized water, the test pieces were washed in ethyl alcohol, dried and then weighed again (*P2*). Calculation of the apparent density expressed in $g/dm^{3.}$

$$(P1 - P2) \times (A \times s \times 102 \times 10\text{-}4) =$$
$$(P1 - P2) \times 100/(A \times s)$$

where *P1* and *P2* are the two weights in grams.
A is the area in dm^2, 1.5 dm^2 in this particular case,
s is the thickness of the layer in microns,
102 is the factor of conversion from dm^2 to cm^2,
10-4 is the conversion factor from microns to cm.

The data pertaining to these tests are given in *Table 4*, where columns 1, 2, 4, 6, 8 indicate the values gauged in the conditions considered standard by us, i.e. using an acid circulation pump and blowing in air*** Columns 3, 5, 7 and 9 give the values obtained with only the acid-circulating pump operating.

The values at 10 A/Ft^2 and 86º F were also given even though only 15 microns (0.6 mils) resulted with the same number of *Amperes-hour* passed. This confirmed the decisive effect of dissolution caused by sulfuric acid at excessively high temperatures. The samples had a very crumbly milky white surface, typical of the oxide layer produced at very high temperatures. The 66º F column can be considered as quality reference value for anodic oxide layers since industries striving for the best quality operate at that temperature.

Examining the data in *Table 4* one can draw the following conclusions:

a) the apparent density of the oxide layer decreases as the current density (i.e. the voltage) increases, all other conditions remaining unchanged. As indicated above, an increase in voltage leads to the formation of larger pores and, thus, to a lesser apparent density;

b) the apparent density decreases as the temperature increases, up to 77º F, since the chemical attack produced by the acid increases along with the temperature, thus producing larger pores;

c) the use of the agitation system increases the apparent density of the layer, thus indicating that smaller pores are formed if the heat generated on the surfaces of the workpieces is dissipated in a better way;

d) a particular trend is noted at a temperature of 86º F. The density of the layer increases as the current density increases to 30 A/Ft^2, after which it decreases again. This is because the dipping times are longer at lower densities thus, the effect of the acid at high temperatures mainly affects porosity: larger pores, lower density of the layer;

***MicroBubbles System "MB," Italtecno S.r.l., Modena, Italy.

e) if 2.32 g/cm^3 is used as minimum limit value for the quality of the oxide layer, the samples produced by using the air agitation are all acceptable with the exclusion of the ones obtained at 86º F, with 10 and 15 A/Ft^2. Without the use of the special system, the quality already becomes poor at 77º F with 40 and 60 A/Ft^2. Simple agitation with the circulation pump is therefore not enough to achieve an acceptable quality. Without the use of the special system, the quality of oxide produced at 86ºC is unacceptable, with the exclusion of that produced with 30 or 40 A/Ft^2, which is, however, very near the limit.

In view of these results and to operate at temperatures higher than the conventional values, we decided to test a series of products able to exercise a protecting effect on the layer of oxide as the temperature increased.

5.3.2. Protective Effect of Certain Additives on the Oxide Layer

It has been known for some time now that certain additives such as oxalic acid for example, allow the anodizing process to be carried out at slightly higher temperatures owing to their ability to slow the dissolution activity of the oxide layer during its formation. Several organic acids of which the protective effect is known and certain industrial products marketed by Italtecno (*WM 80* and *WM 80L*) were compared along with a new product resulting from this research called *HEA additive*, for the sake of simplicity.

5.3.2.1 - Description of the Test

We prepared samples anodized in the usual way (66º F and 15 A/Ft^2). These were first washed in mains water and then in demineralized water, after which they were washed for a few minutes in ethyl alcohol in order to facilitate the drying process. The perfectly dried samples were weighed (*P1*) and immersed in the solutions indicated in column 1 of *Table 5*, where the sulfuric acid solution without additive was considered as a reference.

After the test, the samples were washed in running water and demineralized water and were then immersed in ethyl alcohol for a few minutes to facilitate the drying process. When they had perfectly dried, the samples were weighed again (*P2*) and the weight loss was expressed in mg/in^2 according to the following calculation:

$$(P1 - P2) / 23.25$$

where 23.25 is the area in in^2 of the tested sample.

Amines and ammonium salts were deliberately avoided in this test since their use at an industrial scale poses two types of problem to which an adequate solution must be found if they are to be profitably used:

a) In the presence of aluminum ions and sulfates, ammonium salts cause precipitation of the aluminum sulfate and ammonium $(NH_4Al(SO_4)_2(12H_2O)$ or ammonium aluminum sulfate, the solubility of which is very reduced. This results in the formation of a microcrystalline solid, which must be eliminated by filtering in order to prevent the pumps and exchangers from clogging. The addition of ammonium salts (e.g. ammonium sulfate) was for a long time considered the only way to eliminate the aluminum from anodizing solutions (*30*) until the introduction of resin systems**** The produced ammonium aluminum sulfate can be put to good use in industry in order to depurate waste water, particularly that produced by the tanning industry;

b) The addition of amines (e.g. triethanolamine) can lead to the problems indicated in point (a) if, owing to hydrolysis, there is a formation of ammonium ions. It does in any case create problems with water depuration because the amines are not eliminated by the normal depuration treatment used in an anodizing system. We also avoided using particular organic products, such as formaldehyde for example, that are often proposed by certain researchers (*16, 19*). These products are fairly toxic and must be used with caution, carefully verifying the by-products that form in the anodizing solution, and the effect on the wastewater and the relative depuration problems.

The additives indicated in *Table 5* were used at different concentrations (10 - 20 - 40 g/l) in order to ascertain the most efficient one. This obviously depends on the operating temperature of the solution.

****Freeal, Italtecno S.r.l., Modena, Italy.

Thus, if 20 g/l can be used at 68º F, greater concentrations (e.g. 40 g/l) are required at 77 or 86º F. The best result was obtained by using oxalic acid, but use of this acid involves two important limitations:

a) High running costs owing to high consumption,
b) Difficulty in coloring layers produced in this way since their porosity is much lower.

Our tests allowed us to ascertain that reduced porosity (temperature being equal) considerably slows both adsorption and electrolytic coloring. For this reason, when formulating the *HEA additive*, we had to add a special component that promoted the color intensity of the layer even at the cost of less protection in relation to the aggressiveness of the acid.

Table 5 compares the apparent density of the anodic oxide layer as the temperature of the anodizing solution varied, with and without the addition of the *HEA* additive. All the anodizing tests were conducted with the acid circulating pump operating and with the use of the MicroBubbles System.

As shown in the acid dissolution test indicated in *Table 6*, the addition of the *HEA additive* had a protective effect on the layer of oxide and, thus, the higher apparent density of the oxide layer is a logical consequence. The most interesting thing is that the addition of the *HEA additive* makes the apparent density of the oxide layer particularly good even when high temperatures such as 77 and 86º F are used at high current densities of 40 to 60 A/Ft^2.

Considering that the purpose of this research was to propose a fast anodizing system, we intentionally avoided making measurements at 10 A/Ft^2 because they are not convenient from a plant productivity aspect.

5.3.3. Weight Loss (Acid Dissolution Test)

Table 6 gives the weight loss values, varying temperature and current density, according to general industry standards, ASTM B-680 and *ISO 3210.*

The samples, anodized and sealed as described above, were weighed (*P1*) and immersed in the following solution:

Chromic acid	20 g/l
Phosphoric acid	35 ml/l
Temperature	100 +/- 2º F
Immersion time	15 minutes

The samples were washed in running water and demineralized water, were left to dry in the air and were weighed again (*P2*). The weight loss was expressed in mg/in^2 according to the following calculation:

$$(P1 - P2) / 23.25$$

Where 23.25 was the area in in^2 of the tested sample.

The time that elapsed between the sealing treatment and the weight loss test was kept between 4 and 16 hours, because we previously had verified that *ageing* had a very low incidence on the weight loss result. This was especially following the hot treatment after the impregnation process in the nickel fluoride based solution.

To make the results compatible with each other, the samples anodized at the same temperature were immersed in the phospho-chromic solution at the same time, and the solution itself was changed after each immersion. The maximum limit established by the two standards was 2.60 mg/in^2.

Evaluation of the Results:

a) The addition of the *HEA additive* improved the weight loss values, similarly to what had already occurred with the apparent density of the oxide layer.
b) The higher weight loss values were obtained at longer dipping times or at higher temperatures.

5.4. Color Intensity of the Oxide Layer

One of the basic things to check when using particular parameters in the anodizing process is the color intensity of the anodic layer. For this reason, we tested the electrolytic coloring intensity as the temperature and current density varied.

5.4.1. Description of the Test

The samples for the coloring test were anodized along with the samples used for the apparent density and weight loss tests so that the results were completely comparable. Here again, all the tests were conducted in duplicate, thus the values given in *Tables 7, 8 and 9* are the arithmetical average of the measurements made on two samples for each color tone.The samples were colored in the following conditions:

Utilized Solution:
With tin salts as indicated above

Power Supply

Procedures	*BR 30*	*BR 60*
Direct Current Phase		
Time without current	30 sec.	30 sec.
Ramp-up time	30 sec.	30 sec.
Treatment time	10 sec.	10 sec.
Voltage	5 Volts	5 Volts
Alternate Current Phase		
Negative phase	20 sec.	20 sec.
Positive phase	30 sec.	30 sec.
Ramp-up time	30 sec.	30 sec.
Treatment time	30 sec.	60 sec.
Voltage	7 Volts	8 Volts
Obtained color	medium	dark bronze

BR 30 Results (*Table 8*)
BR 60 Results (*Table 9*)

Coloring intensity was checked by a **SP 68 Spectrophotometer-X-Rite**. The following conclusions can be drawn after an examination of the data given in *Tables 8* and *9*:

a) The coloring intensity increases as the temperature rises,

b) The coloring intensity diminishes as the current density increases,

c) The *HEA additive* improves coloring and, with conditions equal, produces darker tones,

d) Considering the value obtained at 66º F and 15 A/Ft^2 as a reference, the same coloring intensity can be obtained by operating at 30 A/Ft^2 and 72º F, or at 40 A/Ft^2 and 77º F.

e) This data is very important because it shows that when using an appropriate additive at a suitable temperature, the same coloring intensity can be obtained as those obtained with standard conditions (66º F - 15 A/Ft^2).

Table 8 and 9 compare the color intensities as the current density and temperature vary with the use of additives such as the *HEA additive* and *WM 80*.

Conditions being equal, additives of the oxalic acid family give narrower pores and, therefore, make coloring more difficult. The *HEA additive* contains a special component able to positively influence coloring.

The *HEA additive* prevents the formation of the greenish grey tones typical of the presence of oxalic acid, and also aides in the production of the reddish shades much appreciated by certain markets.

Table 8 compares (as the temperature and current densities vary) samples anodized in a solution of sulphuric acid with and without the *HEA* additive and colored medium bronze.

Table 9 gives the same results, with and without the *HEA* additive, but colored dark bronze.

We can therefore confirm what was said of the previous coloring test:

a) The coloring intensity increases as the temperature increases and decreases as the current intensity increases;

b) The *HEA additive* improves coloring and, conditions being equal, produces darker and more pinkish tones;

c) The *HEA additive* eliminates the negative effects produced by the higher current density.

6. Necessary Equipment

The following equipment must be available:

a) Current suppliers of adequate power (e.g. 30 to 60 A/Ft^2), with suitable characteristics (it is, in fact, now known that use of pulsating current improves the quality of the anodic oxide layer and its coloring intensity (*31*).

b) Computerized management of the current supplier in order to pre-set the parameters of the anodizing process, such as current density and required thickness, and stop the process once the required thickness has been obtained.

1. In view of the high current density and low tone/micron ratio, manually timed management of the anodizing process (as currently occurs in the majority of plants) can lead to considerable variations in thickness between one lot and the next. This is particularly true if profiles are different, leading to consequent problems, when it comes to coloring and/or sealing.
2. A device

   that calculates the electrolytic area of the individual lots of profiles.

c) An adequate cooling system specifically designed for the *HEA system*, with a chiller and heat exchanger adequate to support ix.

d) A suitable system to circulate the sulfuric acid, specifically designed for the HEA system, with a pump able to adequately support the HEA system.

e) An aeration system for the solution able to produce a high number of very small bubbles.

Note: The matters discussed in points **(c)** to **(e)** above are of great use when it comes to obtaining an oxide layer of the correct quality. Dissipation by means of the special agitation system and elimination (by means of an exchanger) of the heat generated on the surface of the oxide layer by means of the *Joule effect*, are of fundamental importance if excessively soft or even burnt oxide layers are to be avoided.

7. Experimental Data

All tables and graphs are added as an addendum to this paper, pages 15-25.

Table 1 / Graph 1	Voltage Trends
Table 2 / Graph 2	Anodizing Speed Trends
Table 3	Current Consumption
Table 4	MicroBubbles & Apparent Density
Table 5	HEA Additive & Apparent Density
Table 6	ASTM B-680 / ISO 3210 Weight-Loss
Table 7	Coloring Times
Table 8	Color Intensity (Program BR 30)
Table 9	Color Intensity (Program BR 60)

8. Conclusions

The following conclusions can be drawn from the conducted tests and indicated values.

a) A good quality anodic oxide layer can be produced by operating at much higher current densities than the standard conventional methods currently used in the aluminum industry today.

b) With the HEA system the speed and efficiency of anodic production can be doubled and even tripled. An anodizing speed of *more than 1 micron per minute* must be considered completely possible, if work is carried out in suitable conditions.

c) An increase in the anodizing temperature is not only possible, but advisable, in order to reduce costs (higher temperatures allow lower voltage values to be used and, therefore, a lower consumption of current to produce the anodic layer).

d) The best operating conditions are a result of a balance between temperature and current density. A temperature of 77º F and a current density of 30 to 40 A/Ft^2 are favourable conditions for a perfect coloring intensity.

e) Anodic film formation of 1 to 1.2 microns per minute (approx. 20 microns in about 18 minutes) is extremely interesting from a production throughput point of view.

f) A strong increase in productivity can be achieved without substantially modifying an existing plant. It is, in fact, not necessary to increase the number of tanks.

g) Oxide layers produced at high speed are perfectly suitable for coloring with current techniques, both by adsorption in organic dyes, and by the electrolytic process if tin, nickel and cobalt salt based solutions.

h) Layers produced at high speed are suitable for special electrolytic coloring processes

i) The layers themselves can be sealed without difficulty using one of the current sealing techniques:

1. Hot sealing method,
2. Low temperature impregnation sealing using fluoride and nickel salt based solutions,
3. Nickel acetate or non-nickel medium temperature sealing according to recent progressive technologies

j) The fact that layers produced at high speeds give optimum results in sealing quality tests is further confirmation of the validity of the layers themselves since it is well known that abnormal oxide layers (those produced in incorrect temperature, current density or acid concentration conditions) give a poor sealing quality.

Bibliography

1) EURAS-EWAA - Qualanod Specifications for the Quality Label for Anodic Oxidation Coatings
2) Hoshino et al., Met. Finish. Soc. Jpn., June 1984, 34, (6), 283-8
3) Ebihara, et al., J. Met. Fin. Soc. Jpn., Apr. 84, 35, (4), 205-9
4) Fukuda, T. Fukushima et al., J. Met. Soc. Jpn. Ap. 84, 35, (4), 189-95
5) Fukuda, T. Fukushima, Electrochim. Acta, Jan. 1983, 28, (1), 47-56
6) Plat. Surf. Fin., 1982, 69, (9), 22-3
7) Uemura Kogyo - Pat. JAJ 8325759, Dec. 15, (1975)
8) Strawbridge, D.R. Gabe, A.J. Dowell, Trans. Inst. Met. Fin., 1990, 68, (2), 69-74
9) Ellard, D.R. Cowieson, I.M.F. Conf., Sept. 23-25, (1992)
10) Insulators - Pat. JAJ 8213196, (1980)
11) Fukuda, T. Fukushima, Technocrat, Feb. 81, 14, (2), 39-44
12) Ohkubo, Alutopia (Jpn), 1980, 10, (7), 25-32
13) Tomita, Off. Gaz., 30 Sept. 80, Pat. US4225399, 25 Apr. 79
14) Sasaki - Pat. JAJ805595, 5 Sept. (1974)
15) Hokusei Aluminium Co Ltd - Pat. JAJ7919209, 20 Oct. (1975)
16) Hokusei Aluminium Co Ltd - Pat. JAJ7915011, 28 Nov. 74
17) Tomassi, D. Kozminska, Powloki Oschr. 1984, 12, (1), 24-28
18) Okubo Keigo et al., Kinzoku Hyomen Gijutsu 1988, 39, (9), 512-16
19) Garriga Benitez - Pat. US4526660 02 Jul. 85, Mx Appl. 200240 06 Feb. (1984)
20) Hoshino, S. Matsumoto et al., Met. Austalas., 1984, 16, (5), 10-12
21) Nakagishi, Kinki Aruminiumu Hyomen Shori Kenkykai Kaishi 1989, 139, 1-9
22) Wang, D. Liu, Y. Zhang - Pat. CN 1038132, 20 Dec. (1989)
23) Satoh, Plat. Met. Finish, 1990, 77, (12), 76-80
24) Brace, E. Strazzi, W. Dalla Barba, Alusurface ë94 - Interall Publications Modena (Italy)
25) Brace, P.G. Sheasby, The Technology of Anodized Aluminium, Technicocopy Ltd.
26) Wernick, R. Pinner, P.G. Sheasby, The Surface Treatment and Finishing of Aluminium and its Alloys, ASM International Metals Park, Ohio, U.S.A.
27) Elze, Metall. 1955, 9, 11/12, 458-65
28) Kissin, B.E. Deal, R.V. Paulson, Finishing of Aluminium, Reinhold Publishing Corp., ch.2, 13-31
29) Lenz, Aluminium 1956, 32, 3&4, 126-35, 190-201
30) Tajima, Y. Umehara, Plat, Surf. Fin., 1981, 68, (1), 54-8
31) Colombini, First Int. Conf. on Electrochemistry, Conf. Proc., Luxor (Egypt), 1996, Nov. 26-28
32) Colombini, data being published

Acknowledgements

The Authors consider it only right to thank *C. Colombini (engineer)* and the technicians at *Elca* for their active collaboration in preparing a current supplier and for their useful help in researching a suitable computerized management system able to ensure constant responses and results.

Slide 1

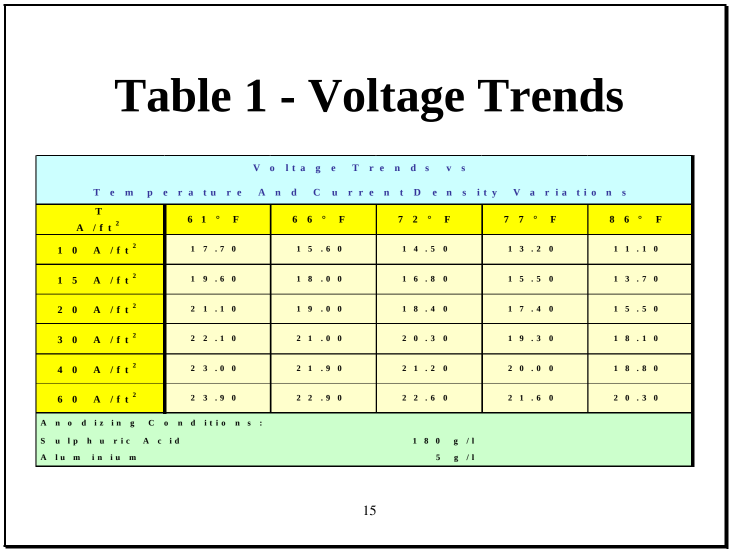


Table 1 - Voltage Trends

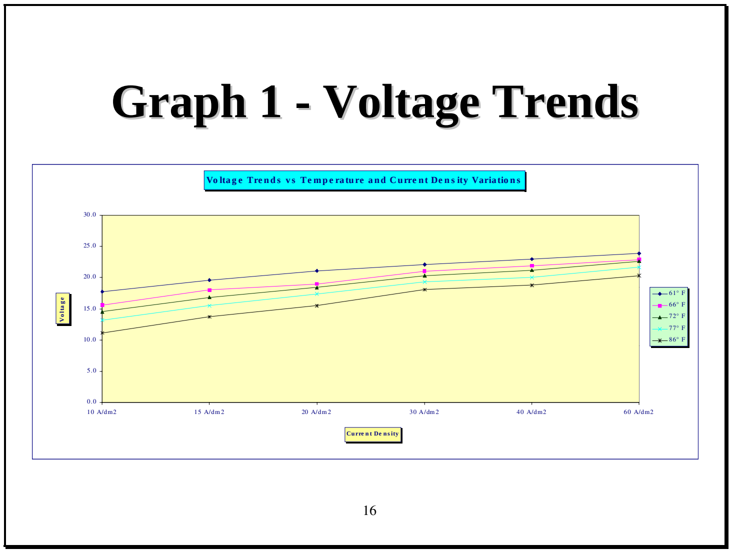
Voltage Trends vs Temperature And Current Density Variations					
T A/ft²	61° F	66° F	72° F	77° F	86° F
10 A/ft²	17.70	15.60	14.50	13.20	11.10
15 A/ft²	19.60	18.00	16.80	15.50	13.70
20 A/ft²	21.10	19.00	18.40	17.40	15.50
30 A/ft²	22.10	21.00	20.30	19.30	18.10
40 A/ft²	23.00	21.90	21.20	20.00	18.80
60 A/ft²	23.90	22.90	22.60	21.60	20.30

Anodizing Conditions:

Sulphuric Acid 180 g/l

Aluminium 5 g/l

Slide 2



Graph 1 - Voltage Trends

Voltage Trends vs Temperature and Current Density Variations

Slide 3

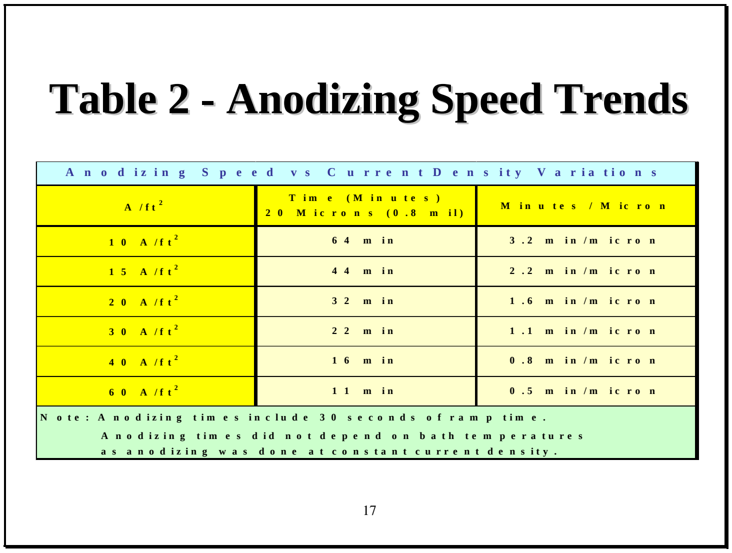


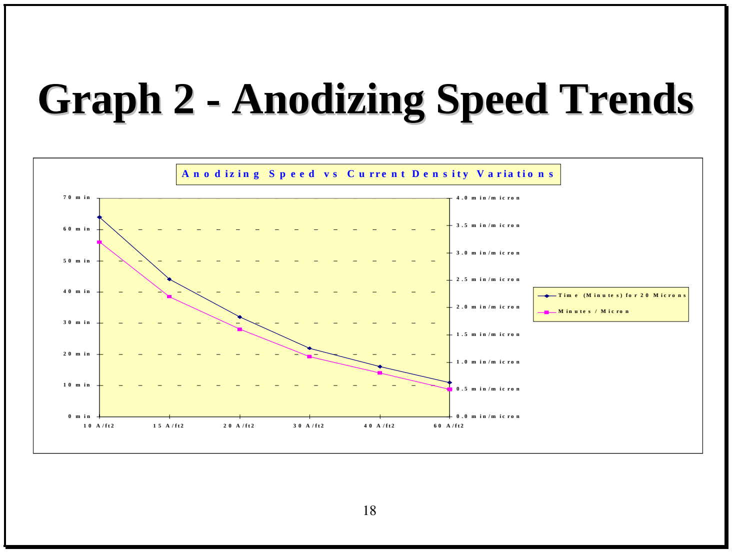
Table 2 - Anodizing Speed Trends

Anodizing Speed vs Current Density Variations		
A/ft^2	Time (Minutes) 20 Microns (0.8 mil)	Minutes / Micron
10 A/ft^2	64 min	3.2 min/micron
15 A/ft^2	44 min	2.2 min/micron
20 A/ft^2	32 min	1.6 min/micron
30 A/ft^2	22 min	1.1 min/micron
40 A/ft^2	16 min	0.8 min/micron
60 A/ft^2	11 min	0.5 min/micron

Note: Anodizing times include 30 seconds of ramp time.

Anodizing times did not depend on bath temperatures
as anodizing was done at constant current density.

Slide 4



Graph 2 - Anodizing Speed Trends

Anodizing Speed vs Current Density Variations

Slide 5

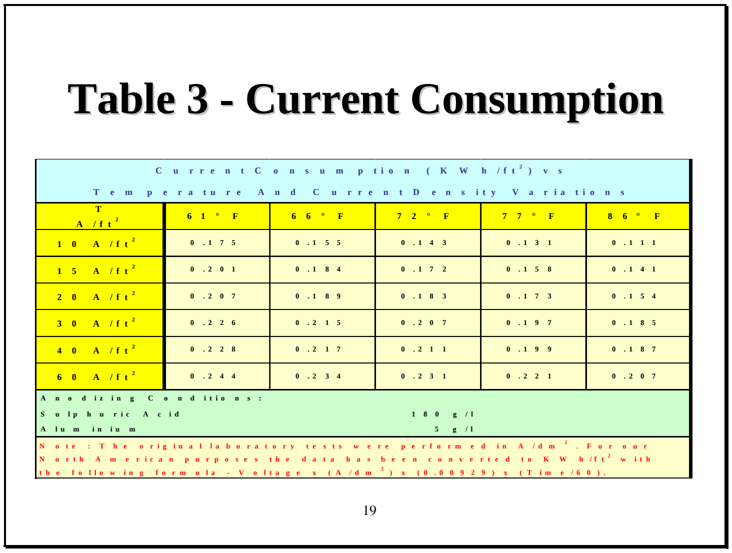


Table 3 - Current Consumption

Current Consumption (KWh/ft²) vs Temperature And Current Density Variations					
T A/ft²	61 °F	66 °F	72 °F	77 °F	86 °F
10 A/ft²	0.175	0.155	0.143	0.131	0.111
15 A/ft²	0.201	0.184	0.172	0.158	0.141
20 A/ft²	0.207	0.189	0.183	0.173	0.154
30 A/ft²	0.226	0.215	0.207	0.197	0.185
40 A/ft²	0.228	0.217	0.211	0.199	0.187
60 A/ft²	0.244	0.234	0.231	0.221	0.207

Anodizing Conditions:
Sulphuric Acid 180 g/l
Aluminium 5 g/l

Note: The original laboratory tests were performed in A/dm². For our North American purposes the data has been converted to KWh/ft² with the following formula - Voltage x (A/dm²) x (0.00929) x (Time/60).

Slide 6

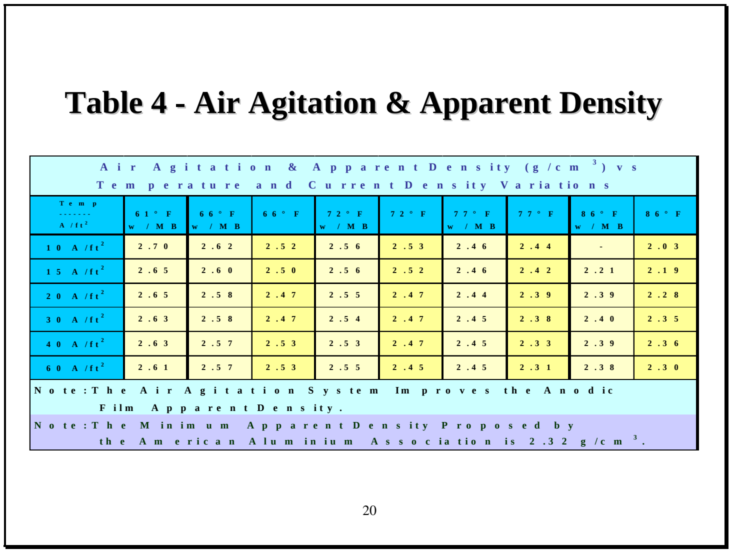


Table 4 - Air Agitation & Apparent Density

Air Agitation & Apparent Density (g/cm³) vs Temperature and Current Density Variations									
Temp ------- A/ft²	61 °F w/MB	66 °F w/MB	66 °F	72 °F w/MB	72 °F	77 °F w/MB	77 °F	86 °F w/MB	86 °F
10 A/ft²	2.70	2.62	2.52	2.56	2.53	2.46	2.44	-	2.03
15 A/ft²	2.65	2.60	2.50	2.56	2.52	2.46	2.42	2.21	2.19
20 A/ft²	2.65	2.58	2.47	2.55	2.47	2.44	2.39	2.39	2.28
30 A/ft²	2.63	2.58	2.47	2.54	2.47	2.45	2.38	2.40	2.35
40 A/ft²	2.63	2.57	2.53	2.53	2.47	2.45	2.33	2.39	2.36
60 A/ft²	2.61	2.57	2.53	2.55	2.45	2.45	2.31	2.38	2.30

Note: The Air Agitation System Improves the Anodic Film Apparent Density.

Note: The Minimum Apparent Density Proposed by the American Aluminium Association is 2.32 g/cm³.

Slide 7

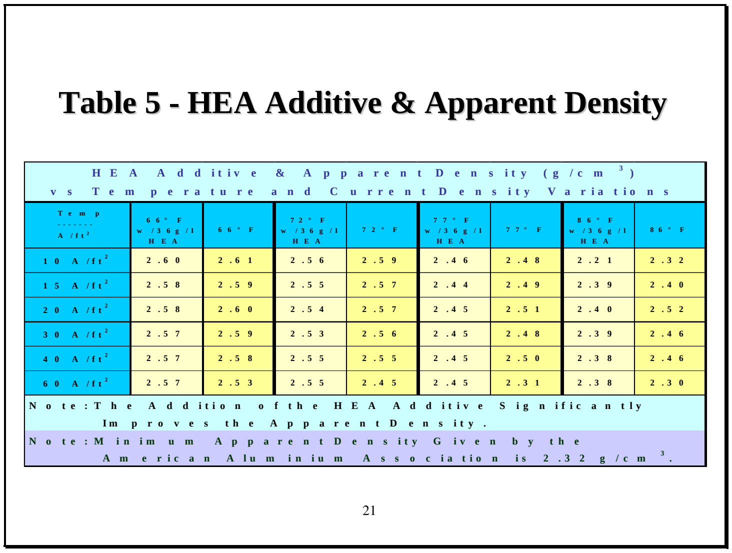


Table 5 - HEA Additive & Apparent Density

HEA Additive & Apparent Density (g/cm^3)
vs Temperature and Current Density Variations

Temp ------- A/ft^2	66° F w/36g/l HEA	66° F	72° F w/36g/l HEA	72° F	77° F w/36g/l HEA	77° F	86° F w/36g/l HEA	86° F
10 A/ft^2	2.60	2.61	2.56	2.59	2.46	2.48	2.21	2.32
15 A/ft^2	2.58	2.59	2.55	2.57	2.44	2.49	2.39	2.40
20 A/ft^2	2.58	2.60	2.54	2.57	2.45	2.51	2.40	2.52
30 A/ft^2	2.57	2.59	2.53	2.56	2.45	2.48	2.39	2.46
40 A/ft^2	2.57	2.58	2.55	2.55	2.45	2.50	2.38	2.46
60 A/ft^2	2.57	2.53	2.55	2.45	2.45	2.31	2.38	2.30

Note: The Addition of the HEA Additive Significantly Improves the Apparent Density.

Note: Minimum Apparent Density Given by the American Aluminium Association is 2.32 g/cm^3.

Slide 8

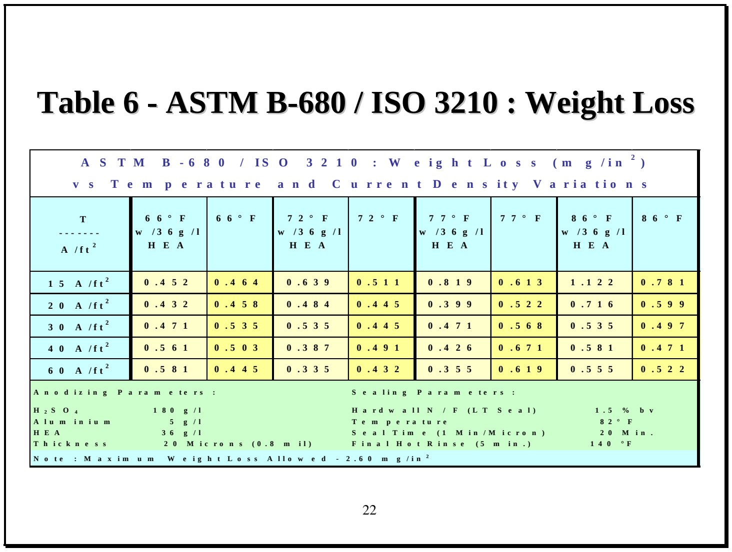


Table 6 - ASTM B-680 / ISO 3210 : Weight Loss

ASTM B-680 / ISO 3210 : Weight Loss (mg/in^2)
vs Temperature and Current Density Variations

T ------- A/ft^2	66° F w/36g/l HEA	66° F	72° F w/36g/l HEA	72° F	77° F w/36g/l HEA	77° F	86° F w/36g/l HEA	86° F
15 A/ft^2	0.452	0.464	0.639	0.511	0.819	0.613	1.122	0.781
20 A/ft^2	0.432	0.458	0.484	0.445	0.399	0.522	0.716	0.599
30 A/ft^2	0.471	0.535	0.535	0.445	0.471	0.568	0.535	0.497
40 A/ft^2	0.561	0.503	0.387	0.491	0.426	0.671	0.581	0.471
60 A/ft^2	0.581	0.445	0.335	0.432	0.355	0.619	0.555	0.522

Anodizing Parameters:		Sealing Parameters:	
H_2SO_4	180 g/l	Hardwall N/F (LT Seal)	1.5 % bv
Aluminium	5 g/l	Temperature	82° F
HEA	36 g/l	Seal Time (1 Min/Micron)	20 Min.
Thickness	20 Microns (0.8 mil)	Final Hot Rinse (5 min.)	140 °F

Note : Maximum Weight Loss Allowed - 2.60 mg/in^2

Slide 9

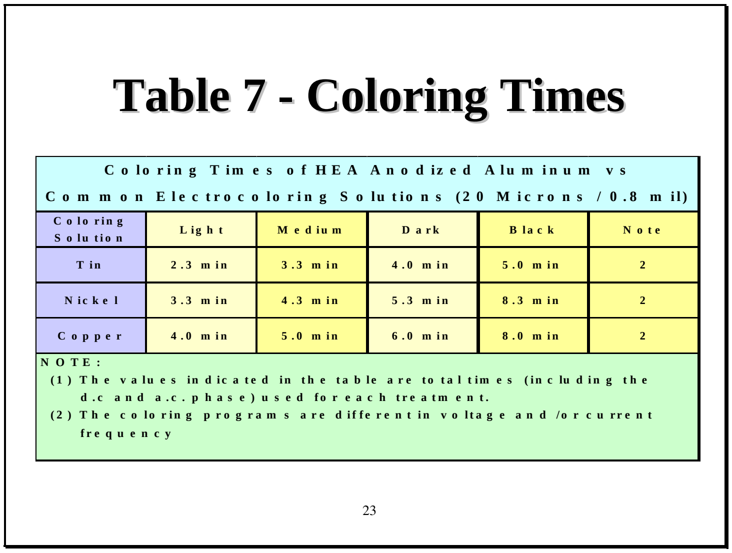


Table 7 - Coloring Times

Coloring Times of HEA Anodized Aluminum vs Common Electrocoloring Solutions (20 Microns / 0.8 mil)					
Coloring Solution	Light	Medium	Dark	Black	Note
Tin	2.3 min	3.3 min	4.0 min	5.0 min	2
Nickel	3.3 min	4.3 min	5.3 min	8.3 min	2
Copper	4.0 min	5.0 min	6.0 min	8.0 min	2

NOTE:
(1) The values indicated in the table are total times (including the d.c and a.c. phase) used for each treatment.
(2) The coloring programs are different in voltage and/or current frequency

Slide 10

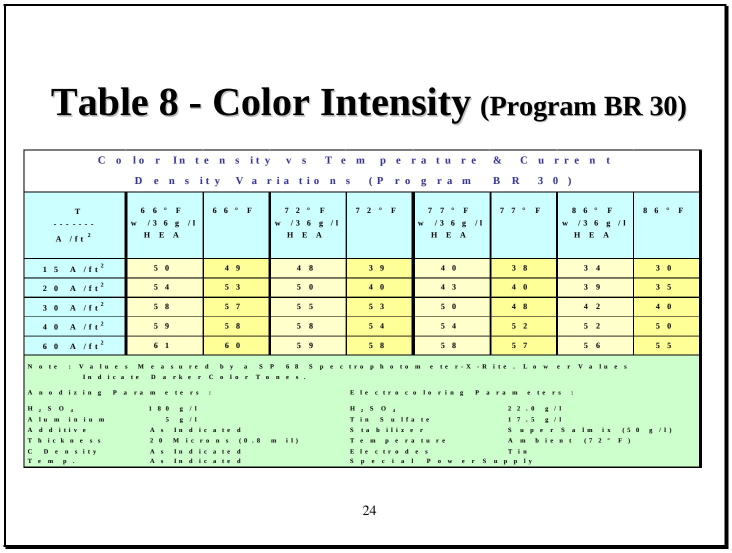


Table 8 - Color Intensity (Program BR 30)

Color Intensity vs Temperature & Current Density Variations (Program BR 30)

T ------- A/ft^2	66°F w/36g/l HEA	66°F	72°F w/36g/l HEA	72°F	77°F w/36g/l HEA	77°F	86°F w/36g/l HEA	86°F
15 A/ft^2	50	49	48	39	40	38	34	30
20 A/ft^2	54	53	50	40	43	40	39	35
30 A/ft^2	58	57	55	53	50	48	42	40
40 A/ft^2	59	58	58	54	54	52	52	50
60 A/ft^2	61	60	59	58	58	57	56	55

Note: Values Measured by a SP 68 Spectrophotometer-X-Rite. Lower Values Indicate Darker Color Tones.

Anodizing Parameters:

H_2SO_4	180 g/l
Aluminium	5 g/l
Additive	As Indicated
Thickness	20 Microns (0.8 mil)
C Density	As Indicated
Temp.	As Indicated

Electrocoloring Parameters:

H_2SO_4	22.0 g/l
Tin Sulfate	17.5 g/l
Stabilizer	Super Salmix (50 g/l)
Temperature	Ambient (72°F)
Electrodes	Tin
Special Power Supply	

Slide 11

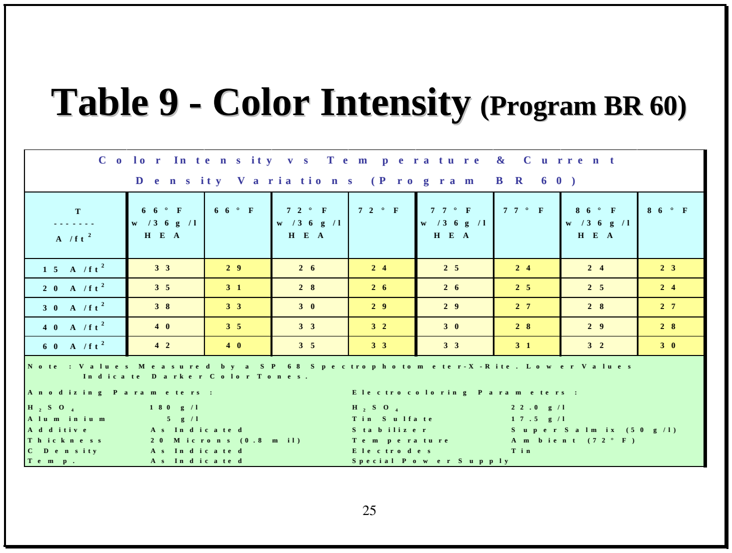


Table 9 - Color Intensity (Program BR 60)

Color Intensity vs Temperature & Current Density Variations (Program BR 60)

T ------- A/ft²	66° F w/36g/l HEA	66° F	72° F w/36g/l HEA	72° F	77° F w/36g/l HEA	77° F	86° F w/36g/l HEA	86° F
15 A/ft²	33	29	26	24	25	24	24	23
20 A/ft²	35	31	28	26	26	25	25	24
30 A/ft²	38	33	30	29	29	27	28	27
40 A/ft²	40	35	33	32	30	28	29	28
60 A/ft²	42	40	35	33	33	31	32	30

Note: Values Measured by a SP 68 Spectrophotometer-X-Rite. Lower Values Indicate Darker Color Tones.

Anodizing Parameters:		Electrocoloring Parameters:	
H_2SO_4	180 g/l	H_2SO_4	22.0 g/l
Aluminium	5 g/l	Tin Sulfate	17.5 g/l
Additive	As Indicated	Stabilizer	SuperSalmix (50 g/l)
Thickness	20 Microns (0.8 mil)	Temperature	Ambient (72° F)
C Density	As Indicated	Electrodes	Tin
Temp.	As Indicated	Special Power Supply	