Title: Let's do it white…... by anodizing!!!!

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Abstract. A chalk-white finishing on aluminum achieved just by anodizing is considered something like a "mirage" or an impossible goal. Now it's possible! A proprietary patented treatment is able to produce a white anodic film on a lot of different aluminum alloys with an aesthetic finishing. The present paper will introduce a new technology that could shake the aluminum finishing market, so long sleeping on "conventional" anodizing and painting processes.
The process is very simple. The pieces are racked and sent directly to the anodizing tank without any preliminary treatment because no degreasing or etching step is strictly necessary and, by using a special power supply, a white film is formed on aluminum just "switching on" the machine.
The process can be applied on high silicon cast alloy, too.
Few microns layer seems to be the best conversion coating on high silicon alloys before any type of painting process (i.e. powder coating, wet paint or E-coat.)
An accurate review of some previous researchers' attempts will be included as an introduction to the proposed process that will be described with data and photos.

Keywords
- **Anodizing,**
- **Alkaline anodizing**
- **White color**

1 - Introduction.

There is a lot of confusion concerning the white color on anodized aluminum, because in literature (patents or papers) words like grey, white, opaque are considered synonymies (or nothing is added to make the subject better understandable). Aim of this paper is to review technologies able to produce a grey or opaque or white color on anodized aluminum distinguishing single step (anodizing in particular solutions) and two or multi-step processes consisting in the deposition of white compounds inside the pores. (*1*). A new feasible technology is indicated to produce an opaque / white finishing.

As shown in *table 1,* it's well known some components of the aluminum alloy can influence the final color of the anodic layer produced in a standard sulfuric acid solutions. *(2, 3)*

Table 1 – Effect of the alloying elements on the aspect of the anodic layer.

Element	Effect
Iron	Reduces the brightness even in small amount. Its addition to pure aluminum leads to dark grey or black streaks, especially when high iron :/ silicon ratio
Silicon	At 5% level alloys, dark grey or black tones are obtained.
Copper	Up to 2% can give alloys with a clear protective coating. At higher level, anodizing becomes more difficult and the coating is softer and with less protective value
Chromium	At 0.3% leads to coatings which are yellow in color.
Titanium	Reduces the brightness, as iron, but is added to produce finer grains
Magnesium	Can give clear colorless coatings up to 3%, probably because magnesium oxide has a reflective index (1.736) very near to that of aluminum (1.69)
Manganese	Up to 1%, Mn may anodize to clear silver, grey brown or mottled according to production process and particles size of the constituents. With thicker anodic films, manganese contents of 0.3-0-0.5% give quite brown anodic oxide coatings on all the alloys.

The subject of this paper will be divided in three mains sections:

a) processes able to produce an opaque / grey film,
b) processes giving pure (or chalk) white color (i.e. without any additional shade),
c) recent or new technologies,

on conventional aluminum alloys suitable for architectural applications. When not differently indicated aluminum pieces are assumed to be subjected to a standard pre-treatment before anodizing; i.e.:

a) alkaline degreasing,
b) alkaline etching,
c) rinsing,
d) acidic de-smutting or neutralization,
e) anodizing in sulfuric acid according to *Qualanod Specifications (4)*

where the alkaline etching dipping time is not considered strictly important even if it's logical that a long dipping time (15-30 min.) giving a matte finishing is able to produce a *stronger* effect or a darker color of the subsequent treatment.

2. Grey / Opaque finishing

Conventionally speaking, the anodic layer produced in sulfuric acid solution on 6xxx aluminum alloys is considered transparent and colorless, and the dipping time in alkaline etching is not significant go give a color tone to a standard thick (10 – 25 micron) film.

When a standard anodic film is subsequently treated in a weak acid solution by a low direct or alternate current, a modification of the barrier layer is produced making it opaque, and the color of the film turns to grey. *(5-7)*. The second anodizing solution can be formed by 0.1-5.0% sulfuric acid and/or organic acids (oxalic, citric, tartaric) or their salts. Low voltage (better if a.c.) and lower temperature are preferred in order to darken the color.

Similar result is obtained with the *Greylox* process (*8)* where the anodic layer is produced in a standard sulfuric acid solution followed by a secondary electrolytic treatment performed in the same solution by the same current supply. The second step is low voltage (< 5 Volt), special frequency a.c. treatment, and color tone is ranging from pearl to dark grey.

A white – opaque coloration is claimed reachable when a conventional anodic film is treated in a solution containing small amounts of nickel sulfate, tin sulfate, tartaric acid and sulphamic acid by means a complex alternate current *(9)*.

In any case, all the grey tones obtained by a second electrolytic treatment can be modified (darkened) by a subsequent coloring in a standard tin-based electro-coloring (or two steps coloring) solution or in an organic dyestuff, obtaining a wide range of color tones.

An opaque film is claimed to be obtained *(10-11)* even when aluminum material is previously anodized in a weak organic acid (tartaric or oxalic), and, finally in a standard sulfuric acid solution.

3. White coloring

Different ways are possible to produce a white *effect* or color on anodized aluminum as:

a) One step or integral white color,
b) Alkaline anodizing,
c) Multi-step coloring.

Special etching steps in alkaline or acid solutions can slightly influence the *whitening* of the final finishing. The white tone is increased if in the conventional alkaline etching solution phosphates or fluorides are added, and nitrates are able to speed up the reaction. This type of solutions should be managed by experienced people because this type of addition reduces their stability.

An acidic etching treatment is not conventional for architectural application, but a composition including fluorinated acids, nitric acids and a suitable metal ion as a catalyzer is able to produce a fine, white finishing on aluminum in few minutes, but large part of the white tone is lost during the anodizing step.

3.1. Single step white color.

A typical example is the *Ematal* process *(12 – 15)* able to produce a milky white, non metallic appearance resembling porcelain enamel. The formulation contains oxalic acid and salts of thallium, zirconium or titanium, and the white color is generated by the metallic hydroxides trapped in the anodic layer. An improved composition can be:

Potassium titanium oxalate	45 g/l
Boric acid	12 g/l
Oxalic acid	1.5 g/l
Cobalt acetate	1.2 g/l
Temperature	60° C
Voltage	110 V

In our laboratory we prepared a proprietary and very simple composition of a titanium oxi-salt solution and we are using it for some specific applications. On high silicon alloys we used the same

machine and “one step” process as described below as “SweetMag ™. Some results are shown in *figure 1-3*

Figure 1- AA 4xxx aluminum alloy pan treated with Ti-based anodizing process.

Figure 2 – AA 5473 Aluminum tiles for anti-slip flooring, anodized using a Ti-based anodizing solution. This type or process offers a ceramic aspect and a good wear resistance because the superficial hardness is higher than conventional anodizing.

Figure 3 – 12% - Si-containing die-cast part after anodizing in a Ti-based anodizing treatment. This type of process can offer a better wear resistance and higher thickness compared with conventional anodizing (quite similar to a hard coat; on that alloy).

Similar opaque coating *(16)* is obtained from the following process:

Chromic acid	30 g/l
Boric acid	1-2 g/l
Current density	0.3 A/dm^2
Voltage	40 – 60 V
Temperature	40 – 55 V

The French *BF4* based *(17)* on a mixture of chromic, oxalic and boric acids is used at 42-48° C, 40-50 V and 0.8 – 1.0 A/dm^2 and 20 micron layer is achieve in about 60 minutes.

A white coating is produced anodizing in a solution of oxalic acid and/or its alkaline metal salts *(18).* Enamel like film is obtained anodizing in the following solution *(19)*:

Sulfuric acid	300 – 350 g/l
Fluorinated acids	2 - 6 g/l
Boric acid	2 – 6 g/l
Current density	8 – 12 A/dm^2
Voltage	40 – 45 V
Temperature	5 – 20 °C

Anodizing in a solution containing:

Alkaline metal acid phosphate	10 – 70 g/l
Citric / tartaric acid	100 g/l
Oxalic acid (or salts) (optional)	1-50 g/l

is claimed to produce a white color, where the addition of trietanolamine can be useful to protect the anodic layer *(20)*

3.2 – Alkaline anodizing

This treatment is not popular but is claimed to be able to produce a white opaque film, that, when obtained in a correct way, has a behavior similar to the standard sulfuric acid layer. Several different formulations containing sodium carbonate, caustic soda with a possible addition of hydrogen peroxide are indicated in literature *(21-30).*

A couple of formulations can be listed for researchers.

Sodium carbonate	25 g/l
Sodium fluoride	10 g/l
Current density	2-4 A/dm^2
Voltage	40-80 V
Temperature	60-70 °C

or

Caustic soda	8 g/l
Hydrogen peroxide	20 g/l
Phosphates	0.5 g/l

Some of these anodic layers can be colored by absorption dyeing.

3.3 Multi-step coloring

In this section, the process able to generate a white color by means of a chemical or electro-chemical treatment applied *after* a standard sulfuric acid anodizing is described. A division of this part is possible:

a) The color is generated by dipping or electrolytic treatment in an aqueous solution containing acids or salts,
b) The color is produced by changing the structure of the standard anodic layer, and finally, by dipping or electrolyzing in a solution of metal ions able to produce white hydroxides.

3.3.1 – Two steps processes

Let's list some of the claimed processes

1) A white film is formed when a conventionally anodized aluminum is dipped in hot water (50-100° C) for 30-50 min. and subsequently anodized again in sulfuric acid (10-30%) at 18-22° C. *(31)*
2) Similarly, the intermediate solution can be nickel acetate *(32).*
3) Aluminum is anodized in sulfuric acid solution in presence of magnesium sulfate (> 30 g/l) and, finally, neutralized in a mild alkaline solution, not containing ammonia. *(33)*
4) A standard anodized material is re-anodized in a solution containing an alkaline metal silicate $M_2O(SiO_2)_n$ 0.005-2.0 g/l with SiO_2 / M_2O ratio > 2 (preferably 2-4) at 150-200 V. *(34)*
5) The anodized aluminum is treated at 150-200 V in a weakly acidic or alkaline solution (pH = 4-10) containing aluminate ion and a metal soluble salt. *(35)* When the aluminate content inside the pores overcomes the solubility limit, aluminum hydroxide is formed and a white color is generated.
6) Similarly, the second solution can contain Ti-complex salts able to enter the pores forming titanium hydroxide and producing a white color. *(36)*
7) The anodized aluminum is subjected to electrolytic coloring step in a solution containing Mg^{++}, and other metallic ions. A magnesium sulfate solution is regulated with magnesium

hydroxy-carbonate and the pH is stabilized by adding boric acid, EDTA, or aluminum sulfate. The degree of whiteness increases with the increasing of the pH of the solution. *(37-39)*

3.3.2. Multi-step processes

In the previous treatments, an intermediate electrolytic step able to enlarge the pores, performed in sulfuric, phosphoric acid or in alkaline solution with caustic soda, sodium phosphate or carbonate is able to increase the white effect. *(40)*

Now, an aluminum piece is anodized in the conventional way and, subsequently, electrolyzed in a solution containing a calcium salt and, finally, in a solution of phosphoric acid. *(41)*.

Similarly, the anodized piece is electrolyzed in a solution of phosphoric acid, and subsequently:

1) in a solution containing boric acid or its salts and, finally, in a solution containing Al or Ti salts *(42)*,
2) in a solution containing ammonium alum.

The use of phosphoric acid solution improves the coloring effect because of an enlargement of the pores as demonstrated for the interference colors, making easier the entrance of metallic ions. With suitable metallic ions inside the pores, a pH increase caused by the current is able to produce their white hydroxides.

An important drawback should be considered: the presence of phosphate ions inside the pores makes the subsequent sealing step very difficult, because it's notorious that the presence of small amount of phosphates is dangerous for the sealing quality.

4. Recent technologies

The Authors have no evidence that any of processes mentioned in the previous paragraph had an industrial application. The main reasons could be:

a) The white hydroxides of metals like as aluminum or magnesium have a poor *covering effect* (the white tone generated is not white or opaque enough to mask defects of the aluminum surface).
b) It's quite difficult to manage Ti ions in order to have stable solutions able to be used in an electrolytic step subsequent to a conventional anodizing.
c) The presence of phosphates inside the pores prevents an acceptable quality of any standard conventional sealing step.

Recently a new type of anodizing process as been introduced and can be mentioned as *plasma or micro-arc anodizing.*

In literature patents concerning this process are really hundreds (and we have a lot of them in several language from Russian to Chinese) and we let the students make their own researches using internet to find articles or patents. We just mention some references of producers of this type of technology *(47-49).*

Micro-arc (or plasma or simply MAO or PEO) anodizing has been introduces essentially to produce a hard coat on metals like aluminum, magnesium, titanium and other, without any aesthetic purpose.

Let's focus on this type of process when applied on an aluminum alloy.

An aluminum piece is anodically treated in a medium alkaline solution containing anions like borates, phosphate aluminates, silicates, fluorides and any cation able to form soluble salts with them a layer can be formed on the metal.

Usually, the solutions are diluted and the current density can range from 1-2 to 20-30 A/dm^2.

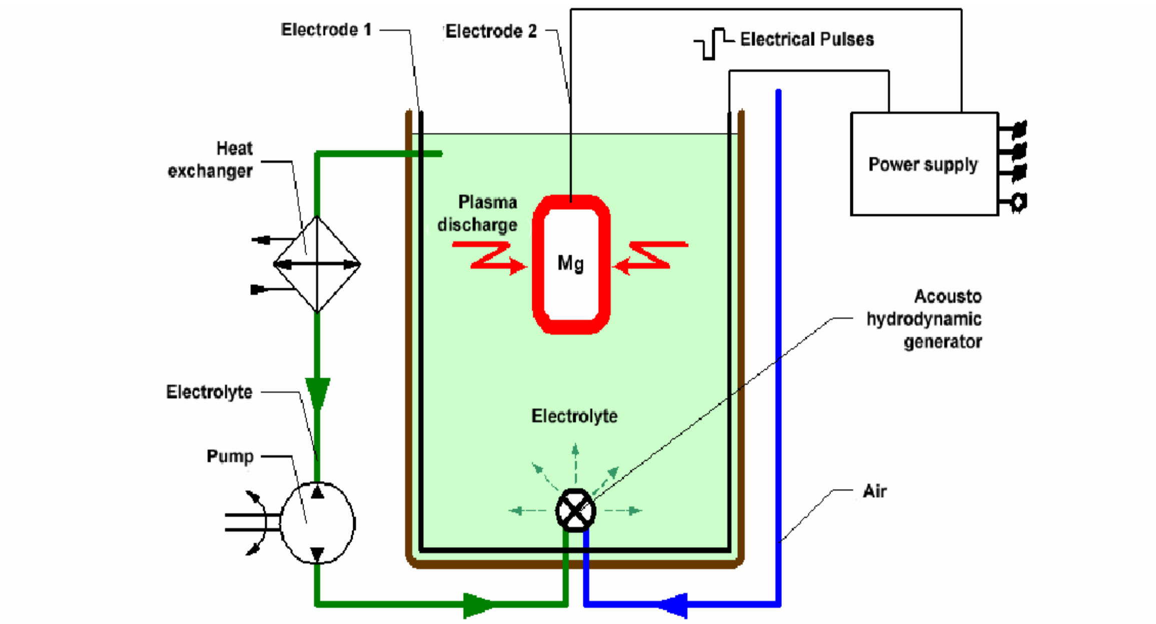

Figure 4- Description of Keronite process (48). In the drawing, magnesium is indicated as treated metal, but process is widely used for aluminum, too.

As shown in *figure 4,* when a high current density is imposed to the piece, a non conductive layer is formed on the pieces, generally acting as anode. With the time passing, the voltage increases to maintain the pre-set current and a *spark effect* starts.
The sparks perforate the formed layer ensuring the conductivity of the system.
Usually sparks start around 150-200 Volt according to the composition of the electrolyte, but ammonia or amine can prevent the effect until about 300 Volts.
Different, simple or complex types of current are used, but the film is mainly formed when to pieces acts as anode.
A typical structure is shown in *figure 5 (50)*

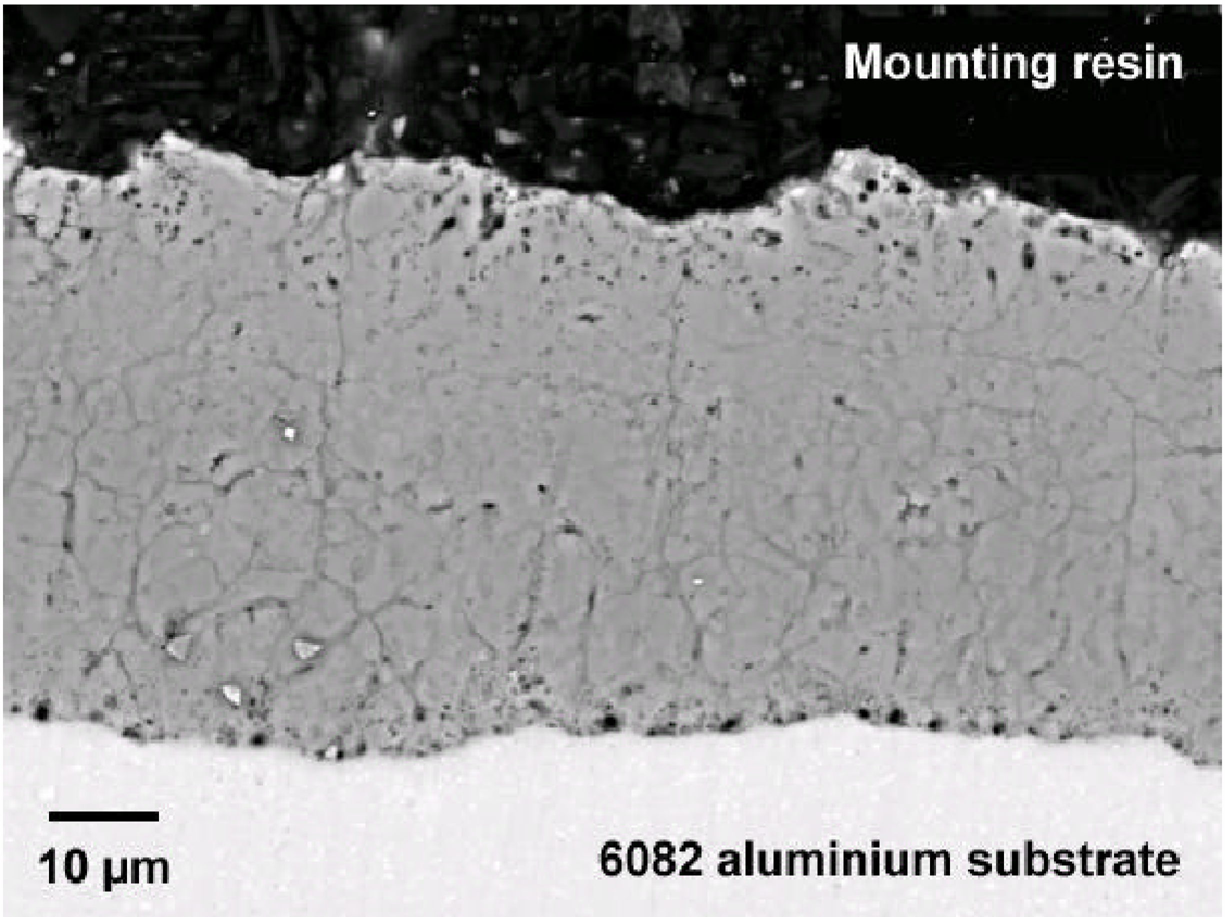

Figure 5 – Back scattered SEM micrograph of a polished cross-section through a 100 µm thick coating on 6082 substrate.

Usually, a micro-arc type layer is essentially formed of an inner part, really hard and compact and an outer, few micron thick layer coarser and slightly more fragile.
In any case the aspect is not transparent, but opaque and white grey.
All the mentioned technologies have been introduced to produce a film harder than a conventional hard coat obtained in sulfuric acid solution. Some of those layers are claimed to reach 2000 HV (when a standard hardness of a conventional hard anodizing on a 6xxx alloy is around 500 HV).

We have no direct information of an aesthetic and/or architectural use of micro-arc anodizing of aluminum, but that could be a reasonable start point.

4.1 – Ours studies

Recently, Italfinish claimed a patent concerning the anodizing of magnesium titanium and aluminum (even when joined together) *(51)*. That process can be considered *one step"* because a piece of one of the mentioned metals is *directly immersed* in a suitable mild alkaline solution and by using a suitable current supply fitted with a proper computerized control board is possible to perform cleaning and anodizing steps in sequence, saving time and chemicals.

Figure 6 – Current supply and its special control board

Figure 6 shows the special machine used for the process.

Our *process*, now registered as *SweetMag*™ because studied and currently applied on magnesium and its alloys, is very simple.
An electrolytic solution is prepared according to a proprietary formulation claimed in the mentioned patent. The aluminum pieces are racked in the conventional way with aluminum or titanium jigs and dipped. As usual with standard anodizing, titanium jugs are preferred when difficult or high silicon aluminum parts as to be processed, to avoid to produce higher thickness on jugs than on pieces. (It happens so if 6xxx racks are used with high silicon parts).
Simply switching on the machine depicted in *figure 3,* the cleaning step and the anodizing step are performed in sequence using a suitable program pre-set in the PLC of the control board of the machine. The process is performed at room temperature at a current density, usually, of 2.0 A/dm^2. Higher current density (e.g. 4.0 – 6.0 A/dm^2 are necessary only when producing thick layers (e.g. 20 micron).
Sealing can be performed in conventional ways (preferably with some new formulation of nickel-based mid-temp type) and the layer passes the weight loss test.
In *figure 7,* a view of our pilot line is shown

Figure 7 – Pilot line used to perform the treatment

When used for aluminum *SweetMag*™, behaves as a plasma anodizing process with strong formation or sparks between cathode and the samples racked as anode as shown in *figure 8.*

Figure 8 – Sparks occurring during alkaline anodizing of aluminum material.

When an aluminum piece, immersed in any mild alkaline solution, is connected to a positive pole of a current rectifier able to supply a constant current for a pre-set time, a low conductive film is formed, because the “dissolving “efficiency” of the electrolyte is very low.
As the layer under formation is compact and low conductive, the voltage will increase to maintain the imposed constant current. When the voltage is about 200 – 300 Volts (it depends on the composition of the solution and operational parameters) “arcing” or sparks between anode and cathode will occur. Sparks are able to perforate the layer under formation and maintaining the conductivity of the system.
We tested different solutions and operational parameters before a very practical choice.
The selected solution can treat almost all the “non-ferrous” metals like as aluminum, magnesium, titanium, and zirconium, but even some of them less conventional like tantalum or hafnium. It’s really a multi-purpose one from this point of view.
The solution is quite stable because all the components are absolutely soluble and difficult to contaminate if a filter pump is used to eliminate any insoluble part.
We preferred a composition able to give a quite smooth finish, because for some application an aesthetic aspect is important, and we matched some customers’ taste.
The following photos are a selection of some of our results

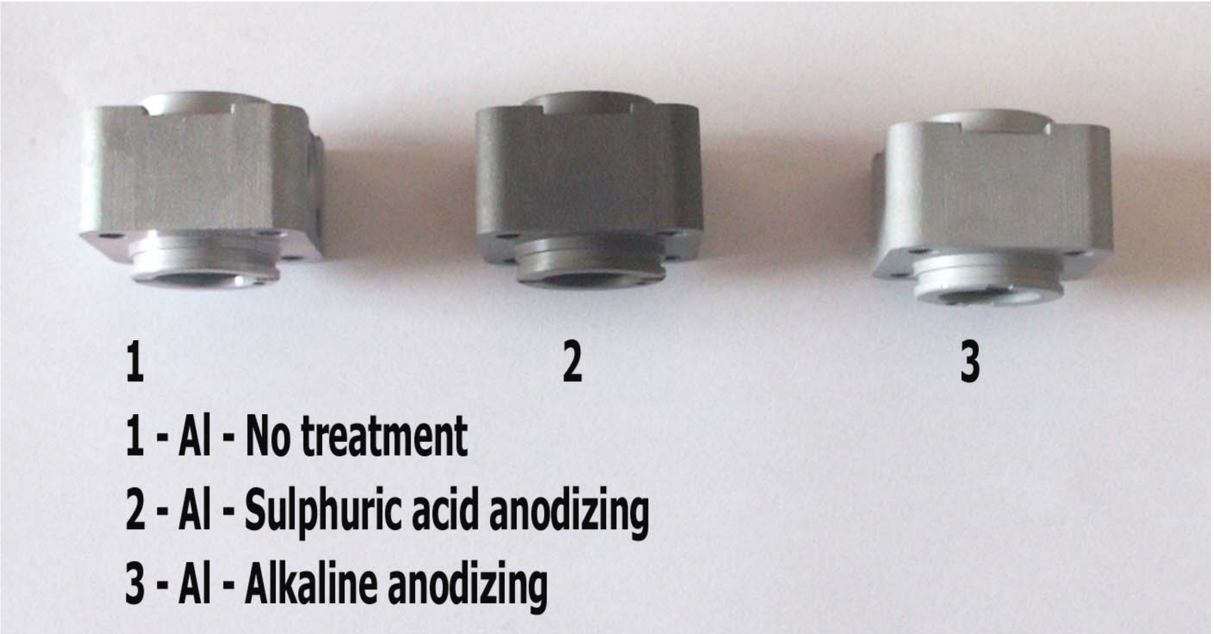

Figure 9 – AlSi12 die-cast alloy anodized aluminum

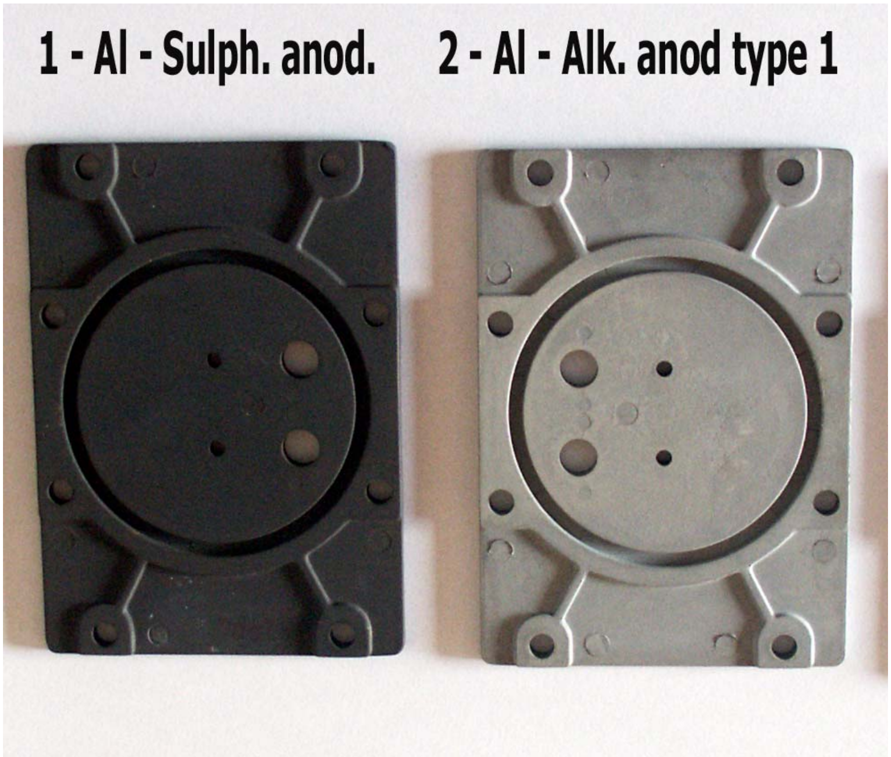

Figure 10 – AlSi12 die-cast alloy anodized aluminum

Figure 11 – AlSi18 die-cast alloy anodized aluminum piston

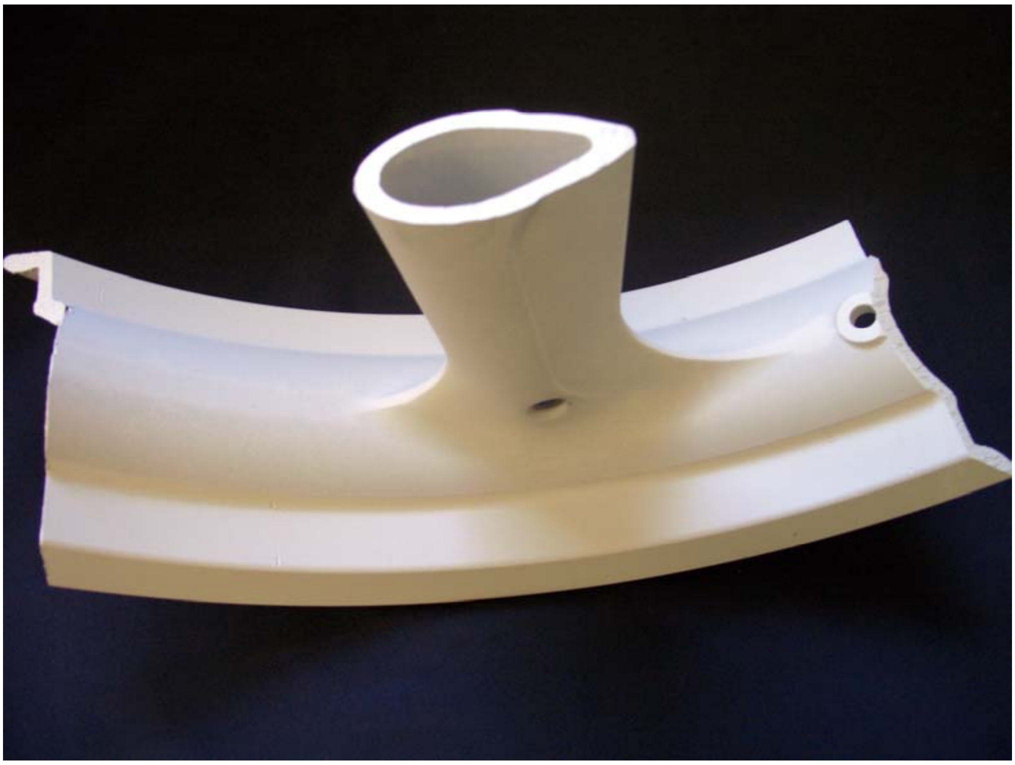

Figure 12 – Part of motorcycle dye-cast wheel after our proprietary alkaline anodizing.

Figure 13 – Hub of the previous wheel after alkaline anodizing and powder coating

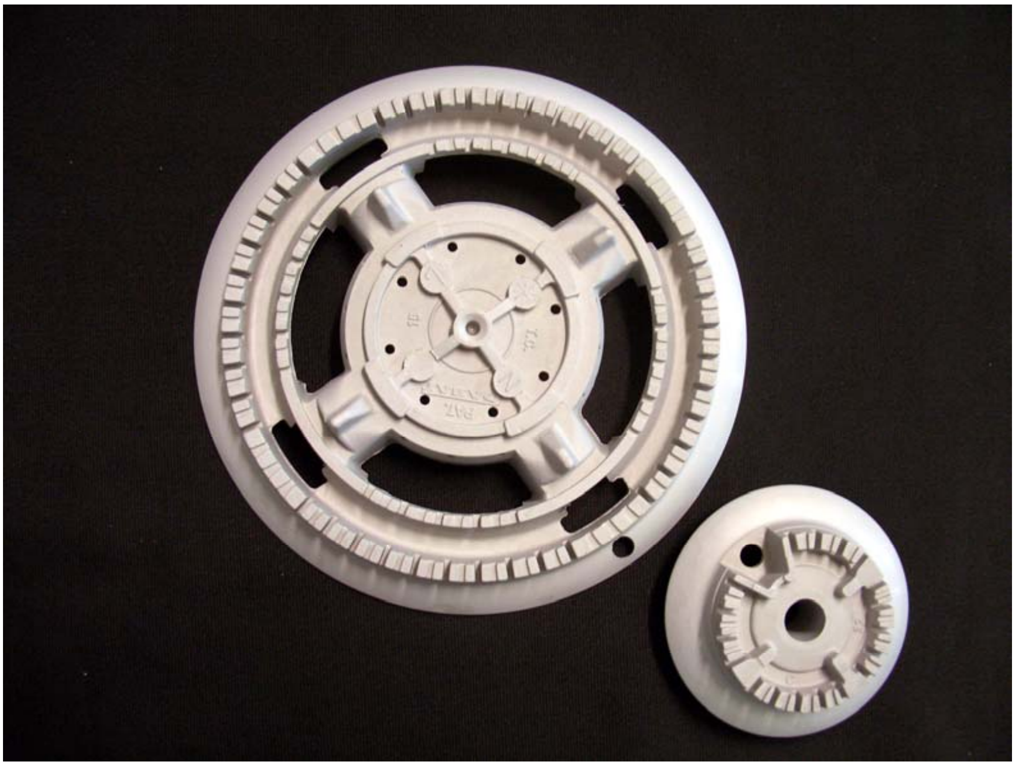

Figure 14 – AlSi12 alloy after our proprietary alkaline anodizing.

Figure 15 – AlSi12 alloy after our proprietary alkaline anodizing.

What is absolutely evident from our tests and from the previous photos is that alkaline anodizing can give a white finishing even on high silicon content.
We gave no real problem to achieve 15 – 20 micron layers even on high silicon dye cast parts. Even the presence of difficult alloying metals like copper or lead has not so adverse effect on thickness or aspect. Even the “marble” effect produced by a not excellent injection step is minimized in alkaline anodizing.
The adhesion of a subsequent paint is excellent and absolutely better than with any other type pf existing conversion coating because no patina or mobile or fragile part is formed or remains on the surface. Excellent finishings are achieved on good quality 6xxx or 5xxxx aluminum parts. The white / opaque tone is evident.

Figure 16 – AA 6082 aluminum mechanical part used, after our proprietary alkaline anodizing

Figure 17 – 1xxx aluminum car parts before and after our proprietary alkaline anodizing

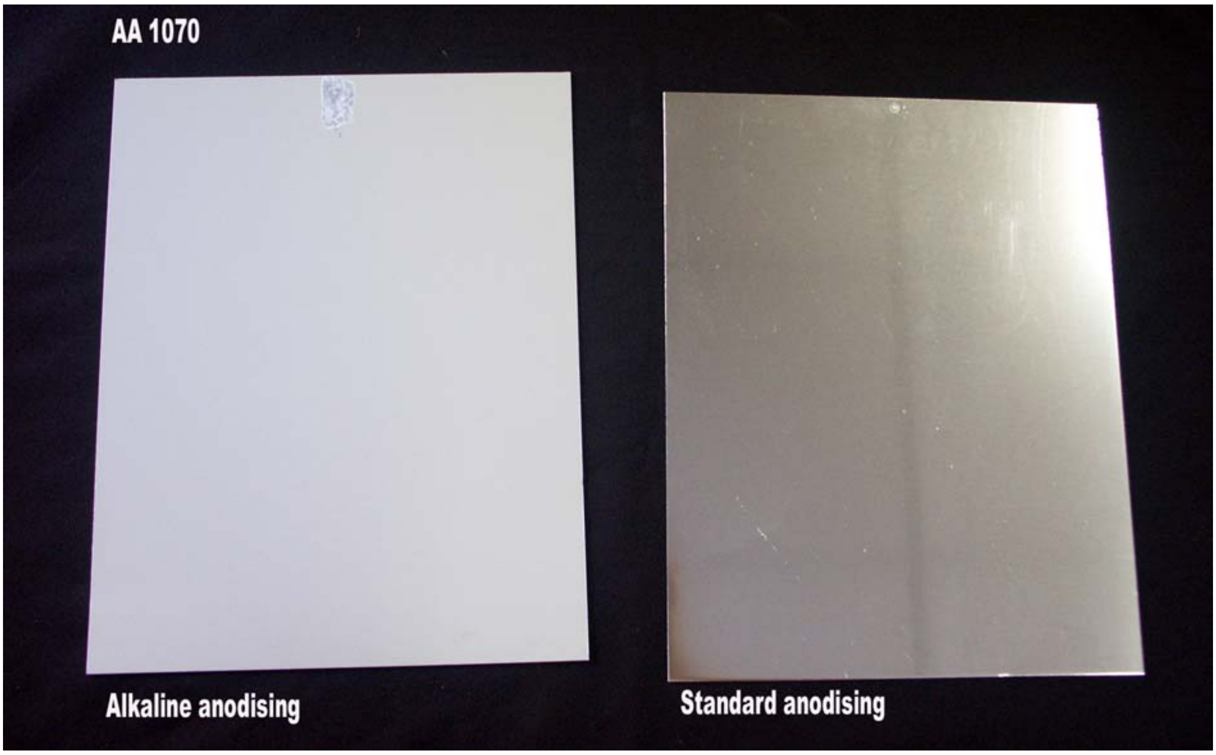

Figure 18 - - Comparison of AA1070 aluminum alloy after conventional and proprietary alkaline anodizing

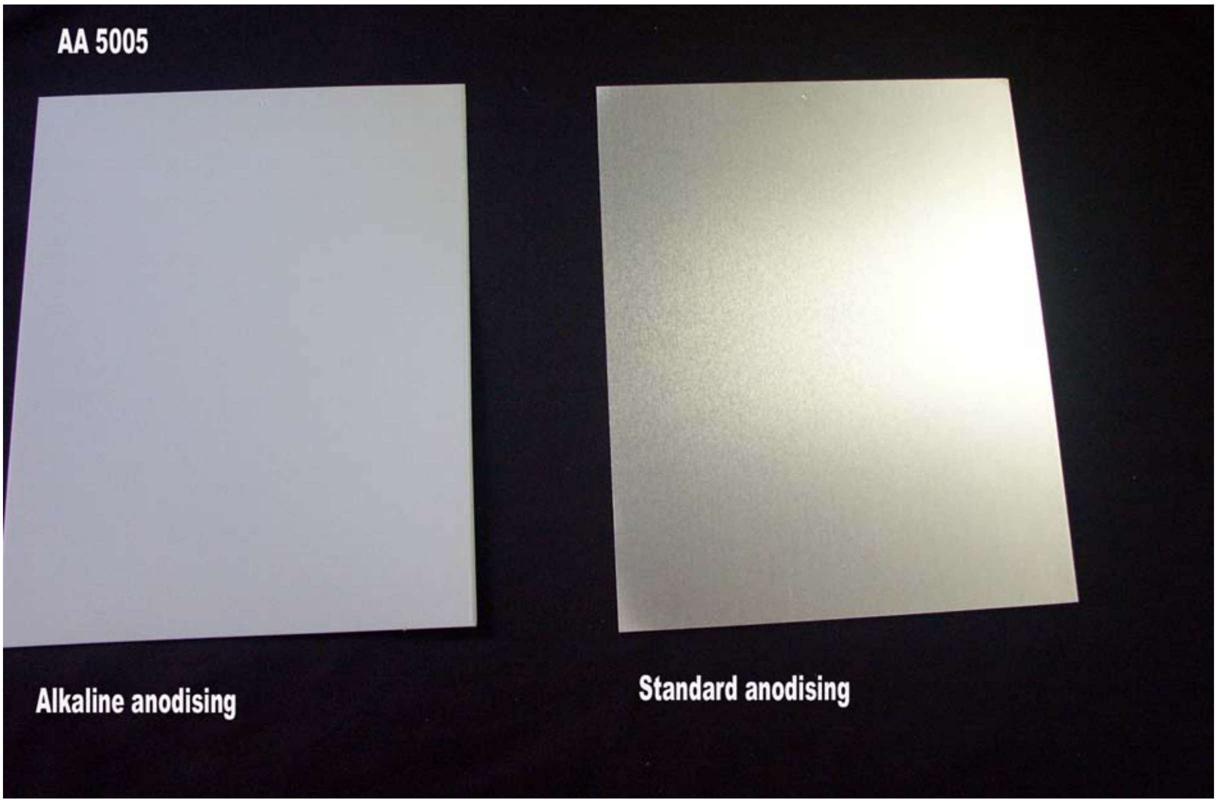

Figure 19 - Comparison of AA 5005 aluminum alloy after conventional and our proprietary alkaline anodizing

Figure 20 - Comparison of AA 6060 aluminum alloy after conventional and our alkaline anodizing

Figure 21 – AA 4xxx aluminum pan after our proprietary alkaline anodizing

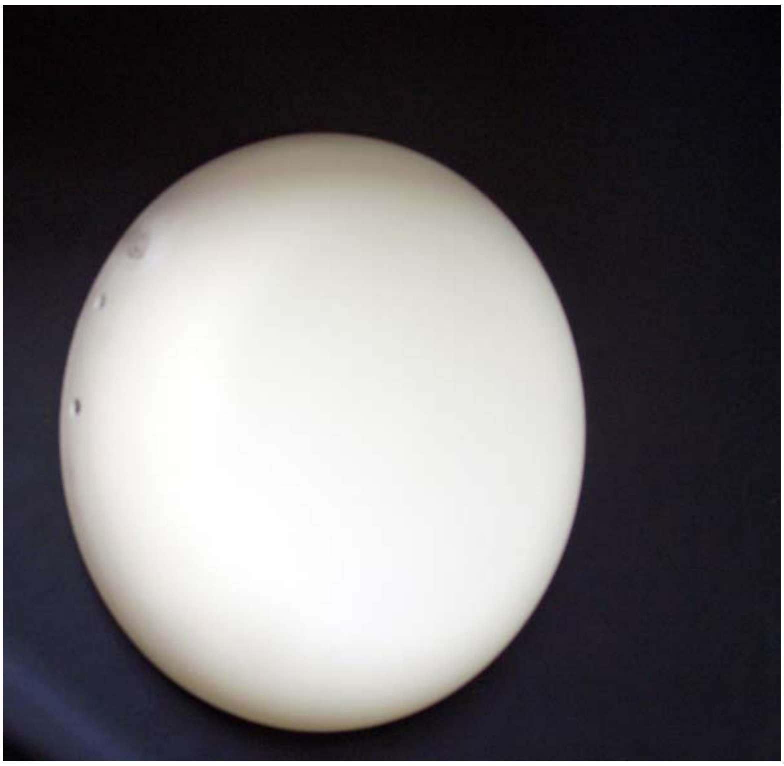

Figure 22 – AA 1xxx aluminum pan after our proprietary alkaline anodizing

Figure 23 – 12% Si alloy piece, after conventional anodizing.

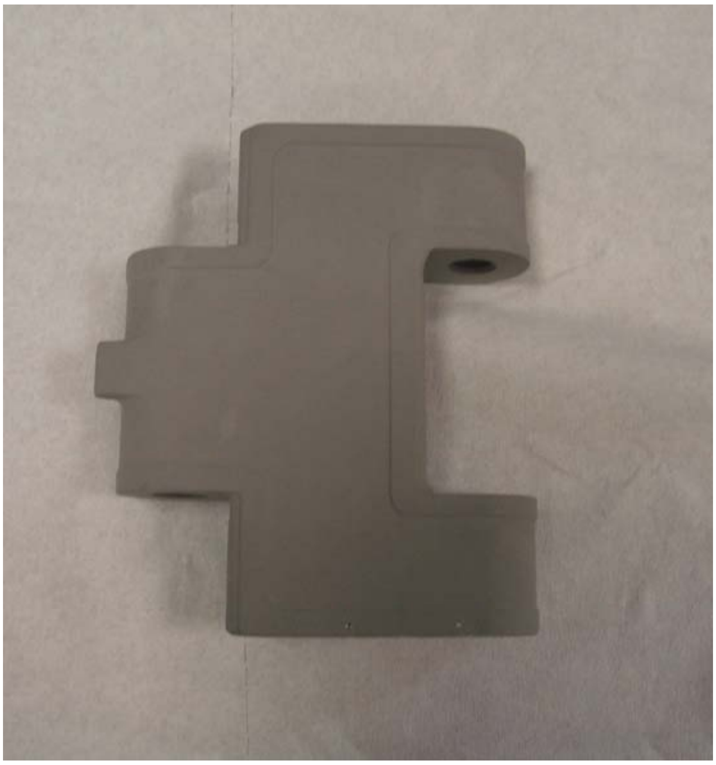

Figure 23 – 12% Si alloy piece, after our proprietary alkaline anodizing. The alloy is exactly the same of the previous photo.

The samples depicted in *figures 16 - 22* show the white / opaque effect achieved using one step process is quite significant. The formed layer has a significant covering effect able to mask even evident extrusion lines. Our quality control tests gave absolutely promising results and they will be continued on specific samples to meet any special requirement from the final customer

4.2 – Some comments

The aspect and color tone depends upon:

a) the type of the electrolyte,
b) the current density,
c) the temperature of the electrolyte.

For this specific aim (i.e. to get a full white covering color we tested even some different electrolytes of those specifically considered in the alkaline anodizing.
Some of mild acidic compositions give advantageous results.
We suggest a room temperature maintained by a suitable heat exchange similar of that used in sulfuric acid process, because the formed heat is significant. Due to the mild pH, the chemical attack of the solution on the layer under formation is not very strong but it’s advisable to dissipate and eliminate the generated heat from the surface in order to avoid a softening of the film. Particular attention has to be paid to the components of the solution if the final step should be a standard sealing process because some of the conventional anions used in alkaline anodizing are dangerous to the quality of the subsequent sealing process.

Some of the white / opaque anodic layer can be colored by dipping or by electro-coloring and the final tone can be attractive.
The formed film can have specific and particular electric characteristics.
Some of the mentioned process can have reasonable costs and the final product should be proposed to the market at a price comparable with a good anodized and colored material.

The white color tone achieved on high silicon containing alloys is worthy for any aesthetic application of them. Few microns of the anodized material performed according to our process is an excellent conversion coating before any type of painting, especially of difficult aluminum alloys.

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