Low energy consumption and environmental friend process for magnesium anodising.

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Abstract
During the last three years, the use of magnesium and its alloys increased sharply because of its light weight and low cost. For many massive productions, magnesium is more convenient than aluminium or zamak (zinc alloy) for many die-cast pieces or items. Magnesium is really sensitive to corrosion if not adequately protected. For many applications a conventional chrome free conversion doesn't give a satisfactory result and anodising remains, probably, the most reliable process both for a "stand-alone" or a painted finishing. Forgetting the old Dow processes because containing chrome, the most common anodising processes, known as micro-arc or plasma anodising require high energy consumption because involving high current density and voltage. As a consequence, production costs are high and the application processes not so simple.
To contribute to the development of magnesium use in mass production items it is necessary make easier and cheaper the anodising process, that at the present time remains the best protection of the metal, with or without any additional treatment.
This paper will describe a low voltage, low energy and spark-free process. able to produce an aesthetic finishing that can be used "stand-alone" or subsequently painted by powder coating, wet paint or, for top class application, even E.D. painted.
Some case studies will be described.

Keywords
- **Magnesium**
- **Alkaline anodising**
- **Silanes-based conversion**

Note. The Authors consider this paper as a "technical" conclusion of their work on magnesium finishing started in 2002 which produced some papers and a couple of patents claiming the disclosed technologies (1 – 4). This paper is focused on the "practical and applicative" aspects of our technologies as a production facility is planned in the close future.

1- Foreword

Magnesium is becoming more and more a partner/ competitor of aluminium in many fields (e.g. automotive)

The reasons are very simple.

- Its cost is quite comparable or lower than that of aluminium. The abundance of natural resources together with the cost effective primary processes contributes to a stable supply that can rapidly grow to meet future demand. The increase in the use of magnesium application is approximately 20% annually. The development of magnesium casting technology, as well as the increasing competitiveness to alternative materials such as zinc, aluminium and plastics is likely to sustain the grow of magnesium casting market for the future *(8)*
- Its weight is 35% lighter even if with the same mechanical properties.
- Extrusion and die-casting can use the same machines or tools of aluminium because the operational parameters are similar for both the metals.
- With a process named "Thixomolding™" *(9)* it's possible to produce very thin parts (below 1 mm) and this is almost impossible with aluminium because forming gas bubbles during casting.

With these premises it is logical magnesium is in quick development in many fields, e.g. automotive, with many projects in progress *(10)* and many groups involved *(11-20)*

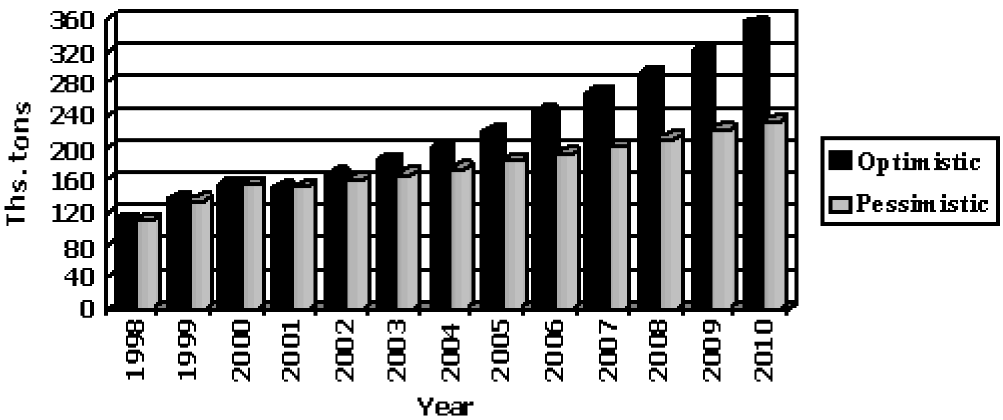


Figure 1 – Perspective of magnesium use for car parts (20)

To help the reader to become familiar with magnesium alloys, in *table 1* the designation method, and in *table 3* the effect of the alloying elements are shown.

Table 1 – Designation of the alloying agents

Letter	Alloying agent		Letter	Alloying agent
A	Aluminium		M	Manganese
C	Copper		Q	Silver
E	Rare Earths		S	Silicon
H	Thorium		Sr	Strontium
K	Zirconium		W	Yttrium
L	Lithium		Z	Zinc

Table 2 – Impact of the alloying agent on the alloy

Element	Impact	Limit (wt %)
Aluminium	Improves strength and hardness. Makes magnesium easier to cast	Upper limit (commercial) 10%, 6% optimum
Beryllium	Decreases the tendency of molten metal to oxidise during melting and casting	Up to 0.001%
Calcium	Assists in metallurgical control. Reduces oxidation in molten condition; improves rollability of magnesium sheets.	< 0.03%
Copper	Improves high temperature strength	< 0.5%, if greater will affect the corrosion resistance
Iron	Can greatly reduce the corrosion resistance, even in small amounts.	0.005% is upper limit, typically
Lithium	Lowers density, improves ductility; improves formability of wrought products. Decreases strength. Limited use.	Up to 11%
Manganese	Increases yield strength slightly. Improves saltwater resistance of Mg-Al and Mg-Al-Zn alloys	1.5%, with aluminium reduced to 0.3%
Nickel	Can greatly reduce the corrosion resistance.	< 0.02%
Rare Earths Metals	Increases strength at elevated temperatures. The narrow freezing range of the alloys reduces weld cracking and porosity in casting.	
Silicon	Increases fluidity in molten states. Decreases corrosion resistance if iron is also present.	
Silver	Increases the response to age hardening.	
Strontium	Increases the strength of die cast alloys at elevated temperature.	
Thorium	Increases creep strength at temperature up to 370 °C	3% on combination with zinc, zirconium or manganese
Tin	Increases ductility when alloyed with small amounts f aluminium. Tin improves properties for hammer forging.	
Yttrium	Added with other rare earth elements to produce creep resistance at temperature up to 370 °C.	
Zinc	Next to aluminium as effectiveness. Used in combination with Al to improve room temperature strength. Helps to improve corrosion resistance.	
Zirconium	Refines grain. Added to alloys containing zinc, rare earths, thorium or a combination of these. Cannot be used with alloys containing aluminium or manganese	4 – 5% in commercial alloys.

Tables 3 & 4 show the composition of a number of magnesium alloys.

Table 3 – Composition of some magnesium alloys for die casting ingots

Type	Al	Zn	Man	Rare Earths	Zr	Si (max.)	Fe (max.)	Cu (max.)	Ni (max.)	Imp.each. (max.)	Imp.tot. (max.)
AZ91A	8.50 - 9.50	0.45 – 0.90	> 0.15	--	--	0.20	--	0.08	0.01	--	0.30
AM60A	5.70 - 6.30	--	>0.15	--	--	0.20	0.04	0.08	0.01	--	0.30
AM50A	4.50 - 5.30	<0.20	0.28 - 0.50	--	--	0.05	0.04	0.08	0.001	0.01	--
AM20	1.70 - 2.50	<0.20	>0.35	--	--	0.05	0.04	0.08	0.001	0.01	--
AS41A	3.70 - 4.80	<0.10	0.20 - 0.48	--	--	0.60 - 1.40	0.04	0.08	0.001	0.001	--
AZ63A	5.50 – 6.50	2.70 - 3.30	0.15 - 0.35	--	--	0.20	--	0.20	0,01	--	0.30
AZ81A	7.20 - 8.00	0.50 - 0.90	0.15 - 0.35	--	--	0.20	--	0.08	0.01	--	0.30
AZ92A	8.50 - 9.50	1.70 - 2.20	0.13 - 0.34	--	--	0.20	--	0.20	0.01	--	0.30
ZE41A	--	3.70 - 4.80	>0.15	1.00 - 1.75	0.30 - 1.00	0.01	--	0.03	0.01	--	0.30
ZE63A	--	5.50 - 6.00	--	2.00 - 3.00	0.30 - 1.00	0.01	--	0.03	0.01	--	0.30
ZK61A	--	5.70 - 6.30	--	--	0.30 - 1.00	0.01	--	0.03	0.01	--	0.30

Table 4 – Composition of some magnesium alloys for ingots for extrusion

Type	Al	Zn	Man	Zr	Si (max.)	Fe (max.)	Cu (max.)	Ni (max.)	Ca (max.)
AZ31B	2.50 - 3.50	0.60 – 1.40	0.20 – 1.00	--	0.10	0.05	0.05	0.005	--
AZ61A	6.80 – 7.20	0.40 – 1.50	0.15 –- 0.50	--	0.10	0.05	0.05	0,005	--
AZ80A	7.80 - 9.20	0.20 - 0.80	0.12 - 0.50	--	0.10	0.05	0.05	0.005	--
ZK40	--	3.50 - 4.50	--	0.45	--	--	--	--	--
ZK60A	--	5.80 - 6.20	--	0.45	0.01	--	0.03	--	--

Having indicated the main alloys, let us now see with which techniques products in magnesium alloys are manufactured.

Similarly to what happens for aluminium the techniques are:

a) Die casting,
b) Extrusion, and
c) Rolling.

Let us now outline the individual techniques more clearly.

1.1 – Die-casting

This is an extremely common method for metals with a relatively low melting point, like aluminium, magnesium and zinc. The advantage of this technique is that even complex shapes with thin walls can be produced accurately.

The drawback is that its use is limited to alloys with a low melting temperature, because those with a high melting one would damage the die. Once removed from the die, the die-casting requires a small number of other operations like deburring, cleaning and final surface treatment.

The die-casting method is the most commonly used one for magnesium alloys, and makes possible to produce a large number of shapes for a vast range of applications.

Figures 2-8 are examples of die cast magnesium and

Figure 2 – Steer column box (Ford), weighing only 340 grams (15)

Figure 3 - Clutch housing (21)

Figure 4 – Motorcycle part (22)

Figure 5 – Nailer casing (22). The piece arrived blasted with evident corrosion pits.

Figure 6 – Scooter wheel (22) The opaque part is blasted and the remaining one is machined.

Figure 7 –PC casing (23)

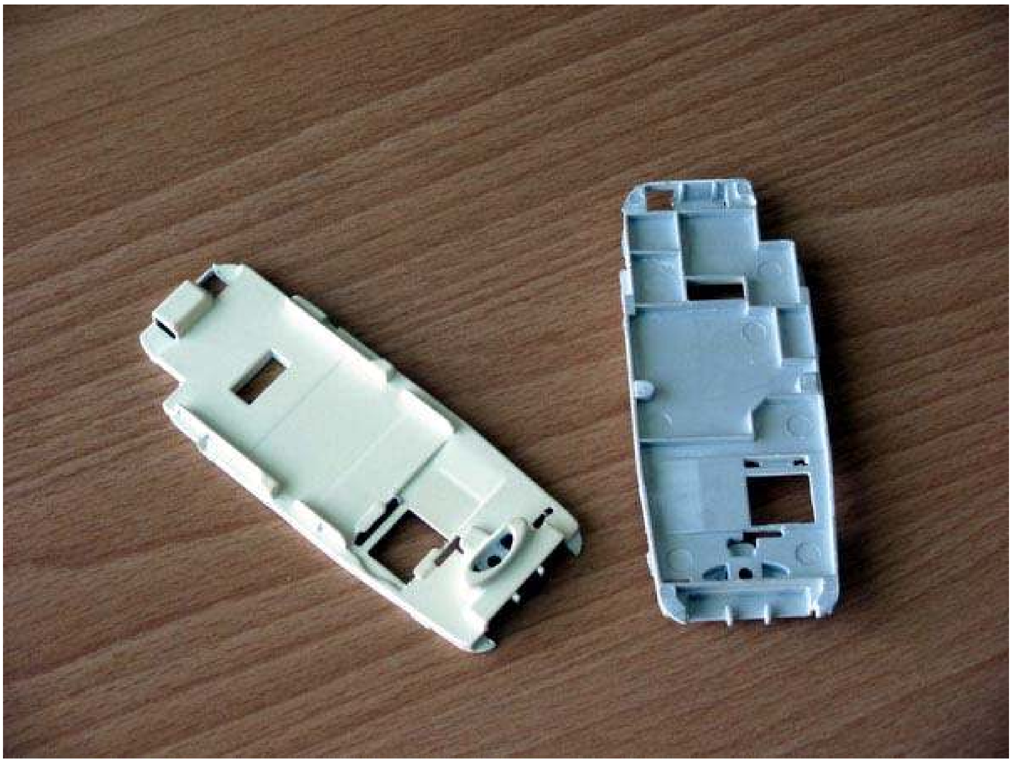


Figure 8 – Cell-phone casing (23)

1.2 – Extrusion of magnesium

The extrusion process of magnesium is very similar of that of aluminium. The ingots of magnesium are transformed in billets and treated in conventional way to produce extruded sections.

Contrarily of what happens with aluminium the type of magnesium shapes are just few and very simple like wires, rods, angles pipes C or U-shapes, etc. as shown in *figures 9 – 10.*

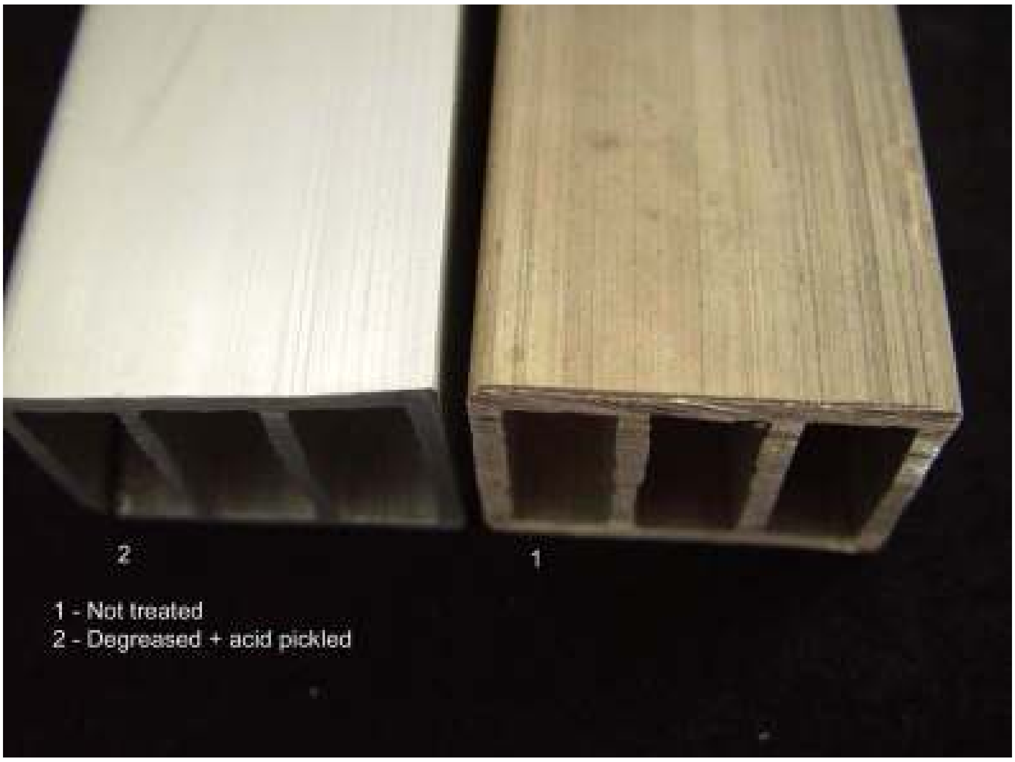


Figure 9 – Examples of magnesium extrusion (22)

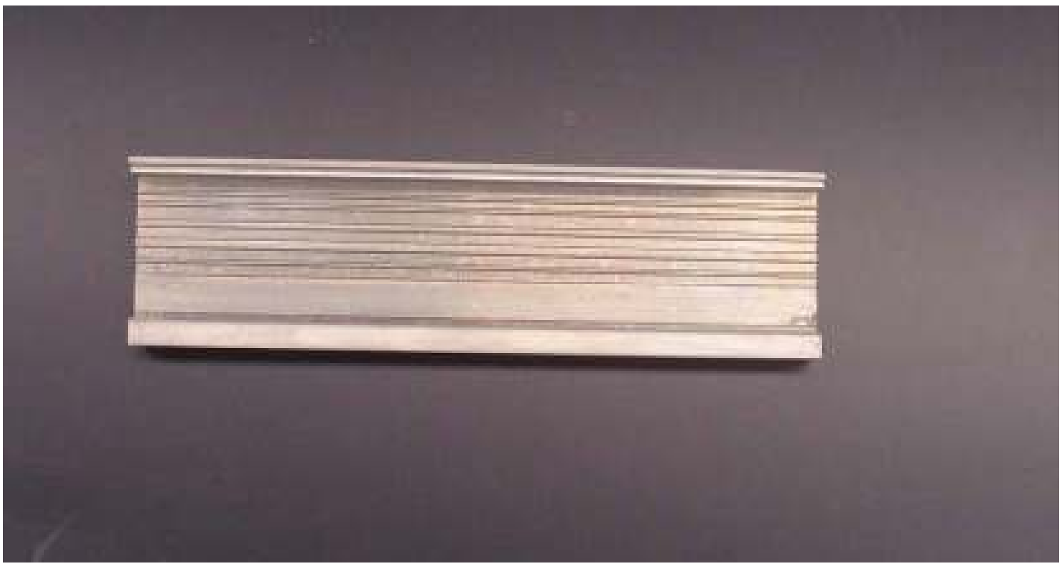


Figure 10 – Examples of magnesium extrusion (22)

1.3 – Rolling

For long time, plates and sheets, even with low thickness were usually produced by extrusion, but now a reliable technology is available for rolling magnesium strips as shown in *figure 11.* An adequate development of this type of technology can widen the applications of magnesium alloys. The day when a car frame will be completely in magnesium is not far, with a strong reduction in weight and, in fuel consumption, therefore.

Figure 11 –Rolling magnesium roller (24).

This type of technology is so important in aerospace and in automotive that suitable chemicals for cleaning and temporary protection of this type of magnesium are already available on the market *(25)*

1.4 - Surface treatments

The resistance to corrosion of magnesium and its alloys is very low and unsuitable for many applications.

In the past 20 years many patents have appeared which claim finishing methods capable of guaranteeing the hardness of the surface films and resistance to corrosion. Part of these patents had industrial application and under its trade mark is listed in our bibliography.

When outdoor exposed, magnesium is usually coated with full covering effect and only for some special applications with "on sight" finishing like in case of cell-phones or laptop casings.
When correctly applied, this finishing is aesthetic and can become and innovative even in automotive field.

The conventional magnesium finishings, usually preliminary to a subsequent painting, are:

1) chemical conversion,
2) anodising.

Important notice. As a regulation in force *(26)* limits the use / presence of chromium salts in automotive, who interested in chemical conversion treatments known as *Dow 1, 19, 21* or anodising ones like *Dow 17 and Dow HAE,* because all using chromic acid in the treatment solutions and chromium (VI) surely remains in the formed layers or coatings. Such treatments, dating back to '40s – '50s, are well know and still included in ASTM and MIL Specs., but the processes we list explain below are not (or less) harmful and, usually, give better results as corrosion and wear resistance.

1.4.1 – Chrome-free conversion treatments on magnesium

Chrome-free conversion coatings for magnesium *(27-30)* are of the same family of those used for aluminium, based on:

a) titanium / zirconium,

b) silanes,
even if treatments with cerium or vanadium salts and alkaline phosphates have been tested.

According to our personal opinion a lot of attention should be paid in the formulation of such treatments because *magnesium is not something similar to aluminium,* therefore, many treatments proposed for magnesium but indicated as "resemblance" or derivation from aluminium are destined to give bad results, especially with low-containing or aluminium free alloys.

A treatment using Ti / Zr salt is sketched in *figure 12.*

Figure 12- Conversion coating on magnesium (29)

Honestly speaking the result obtained with this type of treatment is not always satisfactory and largely dependant on the type of alloy and piece

The best results (after painting) are produced by silane-based chemicals.
The Authors recently worked on the application of *water soluble and hydrolysed silanes* of conversion coating of metals, including magnesium. *(7, 31)*

A serious contribution to the development of the application of silanes as conversion coating on metals is given by *Prof. W.J. van Ooij and his co-workers at Cincinnati University* with an incredible number of patents *(32)* and papers *(33-38),* part of them are available directly at the website of the University. *(34).*

A relevant contribution to the use of silanes in magnesium finishing is given by *Ilya Ostrovsky* with some patents *(32)* which became industrial products of wide use *(30).*
The main advantage of this type of treatment is that can be applied on a wide range of metal substrates with some minor modifications to the pH of the solution.

The basic mechanism structure of a silane treated metal is sketched in *figure 13. (38)*

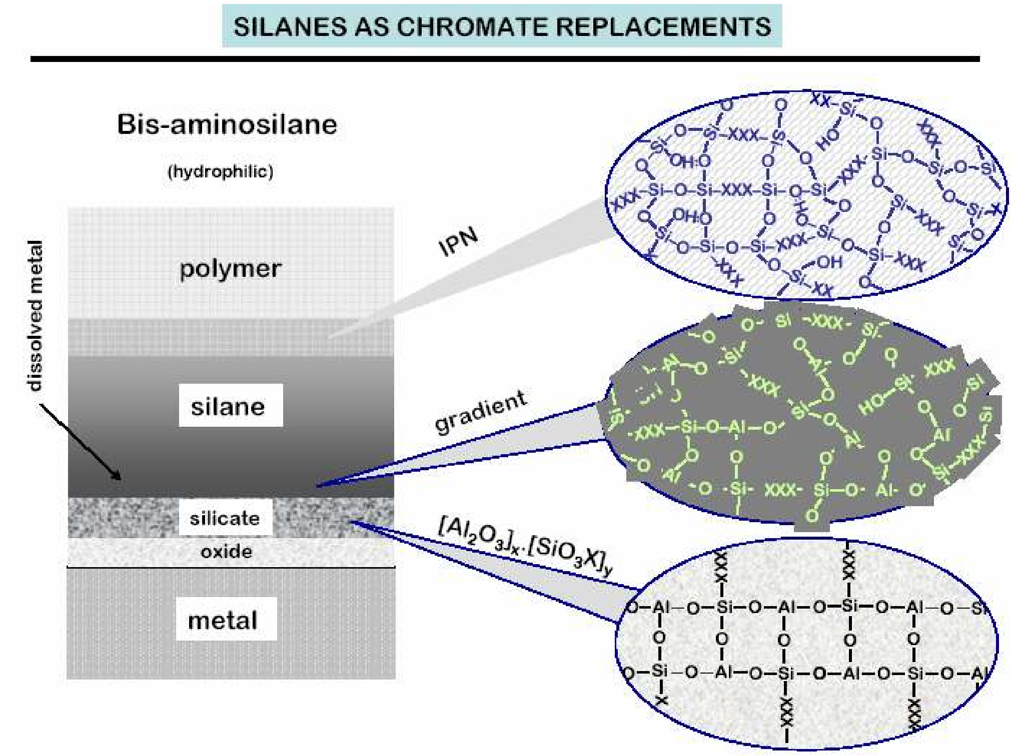


Figure 13 – Structure of a silane-based conversion followed by paint (38)

More recently the "concept" of "super-primer" was introduces
This term is in literature by Prof. W.J. van Ooij and collaborators *(37, 39)* proposing to mix silanes and primers into novel primer systems that combine the properties of both and don't need a conversion coating step.
An exemplary "super-primer" includes a composition capable of coating a substrate and curing to provide a hydrophobic film inhibiting corrosion. *(39).* The composition comprises:

a) a mixture of silanes,
b) a dispersible or soluble resin,
c) an aqueous or non-aqueous solvent.

Figures 14- 16 show, schematically, the concept.

The importance of this type of result is quite evident if we think that for a lot of coil coating processes no preliminary conversion coating is necessary. As mentioned above, magnesium coil will have an important future, because a pre-coat sheet can be formed in the final shape without damaging the external coat to which a final top coat can be added as a final step.
The super primer can act even as top coat assuming pigments are included and a long list of "compatible" components are available.

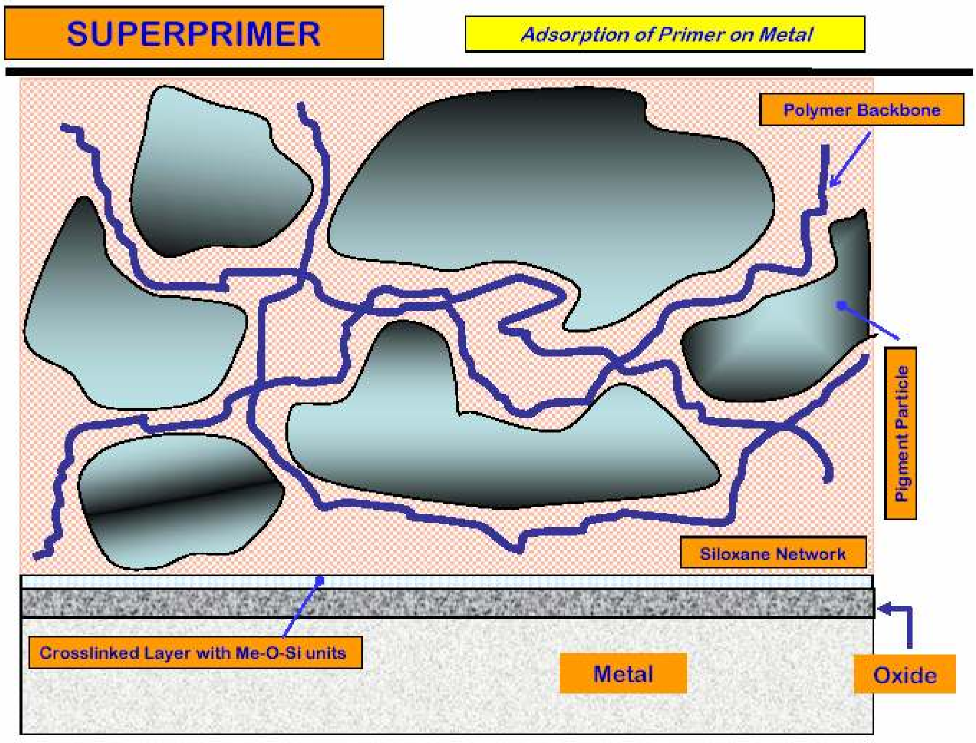


Figure 14 - Mechanism of a "super primer" (38)

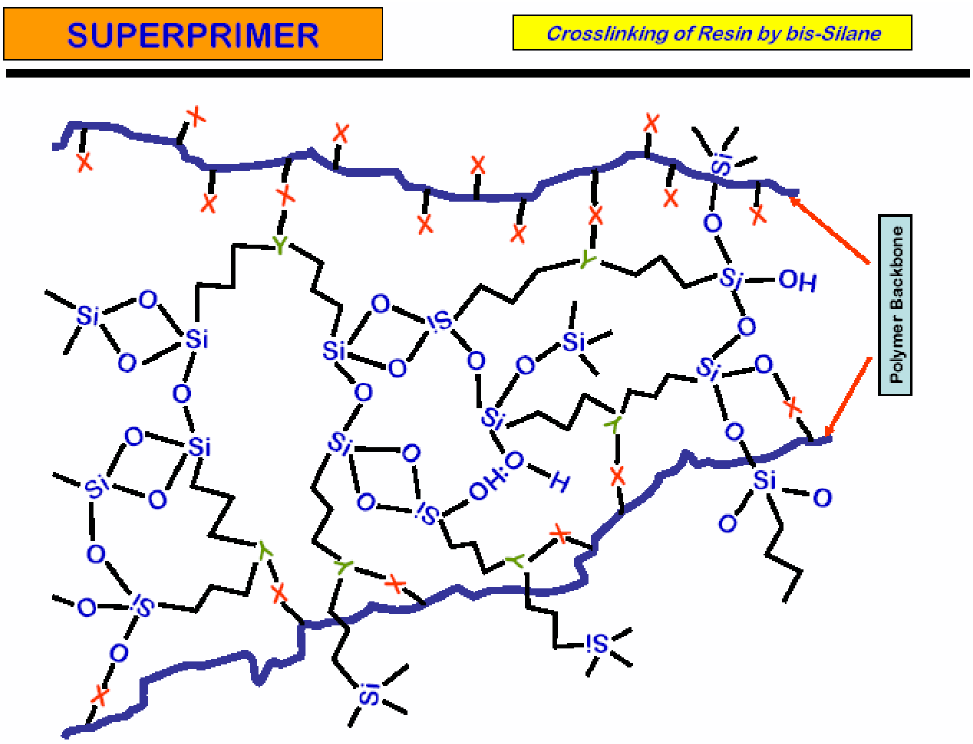


Figure 15 - Mechanism of a "super primer" (38)

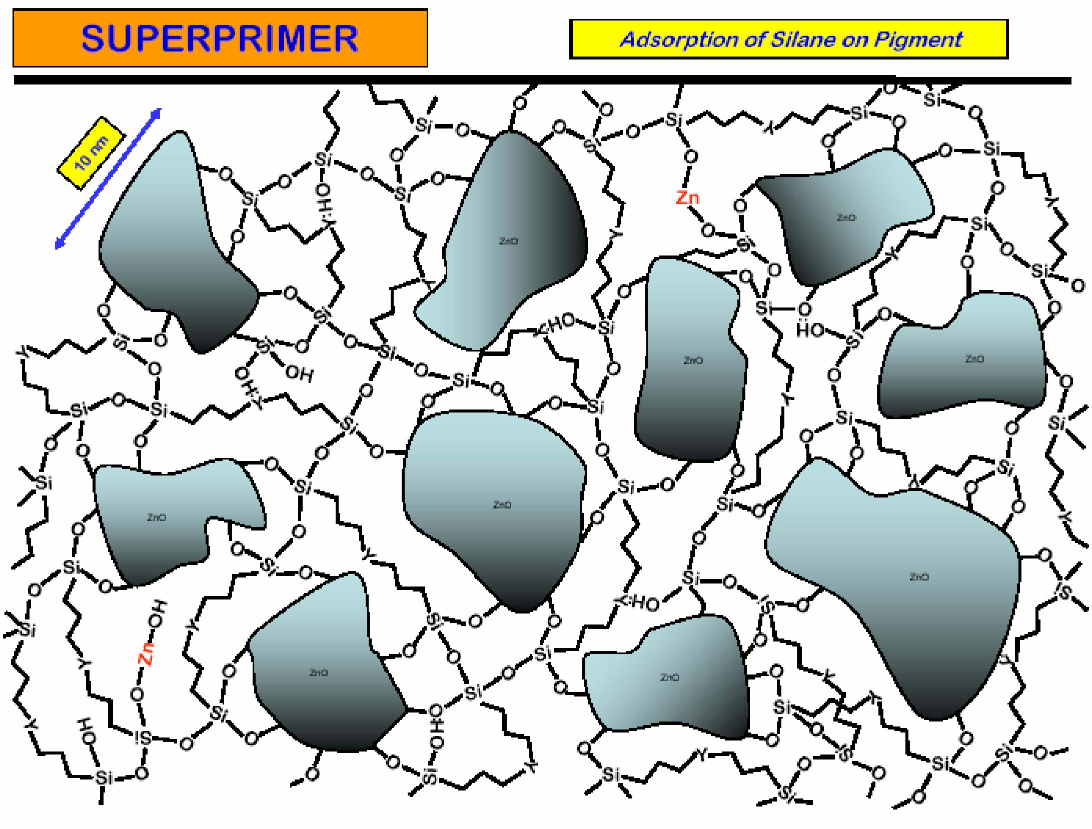


Figure 16 - Mechanism of a "super primer" (38)

1.4.2 – Anodising magnesium

Even when alloyed with other metals, magnesium remains a very reactive metal, especially in presence of acids or in corrosive environments, in general. In these situations, therefore, the above mentioned conversion coatings, even when correctly applied and followed by a good paint, are not always suitable to protect the materials against the corrosion. To protect better magnesium materials and improve the adhesion of a subsequent paint, a method to form, under current, a "composite" layer, which can be over 20 micron thick, has been studied.

When a magnesium piece is immersed in an alkaline solution containing ions able to react with such a metal, and connected to a positive pole of a current rectifier, a dense non conductive layer is formed on the metal. Its composition depends on the composition of the solution and its thickness is related to the passed current.

The operative complexity and toxicity of *Dow HAE and Dow 17* processes and the not excellent corrosion and wear resistance of the pieces treated in that way persuaded the researchers to propose new technologies.

A typical layout of an anodising process for magnesium is as follows.

a) Alkaline degreasing
b) Rinsing in running water
c) Acid pickling
d) Rinsing in running water
e) Anodising with direct or alternate current
f) Rinsing in running water
g) Rinsing in de-ionised water
h) Rinsing in warm de-ionised water
i) Sealing (usually by lacquering)

Generally speaking all the treatments considered in this section are chrome-free, low toxic and offer the following properties:

1) Colourless films
2) Mild alkaline treatment solutions
3) Good adhesion to paint or lacquer
4) Good or excellent corrosion resistance (according to the type of treatment)
5) Good or excellent abrasion and wear resistance (according to the type of treatment)
6) Use of direct or alternate current at high voltage (150-600 volt) and, in some case, high current density.
7) In some cases, a "spark effect" occurs with strong luminescence all around the pieces under treatment, due to a lot of sparks reaching them and producing a complex hard layer containing not only magnesium oxide, but also various different compounds according to the actual content of the solution.

There are on the market some well known processes, and the reader can refer to their websites for the basic technical features *(30, 40-43)*. For a more scientific approach the related patents are available even because some process is over 10 year old. *(32)*. This subject will be studied more extensively in *§ ……*

1.4.3 – "Final" treatments

Both conversion and anodising treatments almost never can be considered "stand alone" for magnesium because their aesthetic and corrosion resistance are not excellent and a further final treatment should be applied.

Painting is the most common of these treatments and, similarly to aluminium, can be:

a) Powder coating,
b) Wet paint,
c) electrophoresis.

Painting can be applied with similar aesthetic results on conversion coating and anodised layers. The corrosion behaviour can be different and usually an anodising process performs better.

2 – SweetMag™ Process

SweetMag™ a new anodising process for magnesium alloys characterised by the following features:

- No pre-treatment is necessary (i.e. the magnesium pieces is immediately treated in the anodising solution)
- No harmful or toxic components are present in the electrolytic solution.
- The solution is long-life and easily maintained by simple additions of the consumed chemicals.
- A simple chemical control can ensure the correct concentration of the chemicals.
- The components of the solution are basic chemicals that can be purchase on the market.
- The process is energy saving because working at low current density and, consequently, at low voltage) compared with similar processes of industrial use).
- The production cost is 1/3 of that of one of the most popular processes available on the market.
- The process can be full automatic and manpower is necessary only for racking and un-racking the pieces.
- The same process, with the same solution can be used even for aluminium, titanium and zinc alloy alloys.
- Different magnesium alloys can be treated with no modification of the operational parameters, and mixed even in the same load.
- The finishing is smooth, even has aesthetic quality.
- The finishing can be used as "stand-alone" (i.e. with no additional treatment).

- The formed layer is suitable for wet paint or powder coating.
- The formed layer is suitable for an electrophoretic (ED) paint with any of the processes available on the market.

To help the reader to understand completely the features of our process, it's better to give some basic information on the anodising process when applied in alkaline solution.

2.1 – Anodising process

Anodising process is a standard treatment for aluminium and its alloys and is conventionally performed in sulphuric acid solution. For this reason still a lot of misunderstandings happen when talking about magnesium anodising. *Magnesium and aluminium are quite different metals from a chemical point of view. If magnesium is immersed in any acid solution, it dissolves forming a magnesium soluble salt and producing hydrogen gas.* The reaction is very strong.
Magnesium is anodised in alkaline solution.
In theory, any alkaline solution can for a layer on magnesium alloys, but in the industrial practice the chosen anions are those able to form chemical complex or salts with magnesium. The cation has a minor influence and is chosen among the alkaline ions or ammonia.

When a magnesium piece is anodically treated in a medium alkaline solution containing anions like borates, phosphates 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.

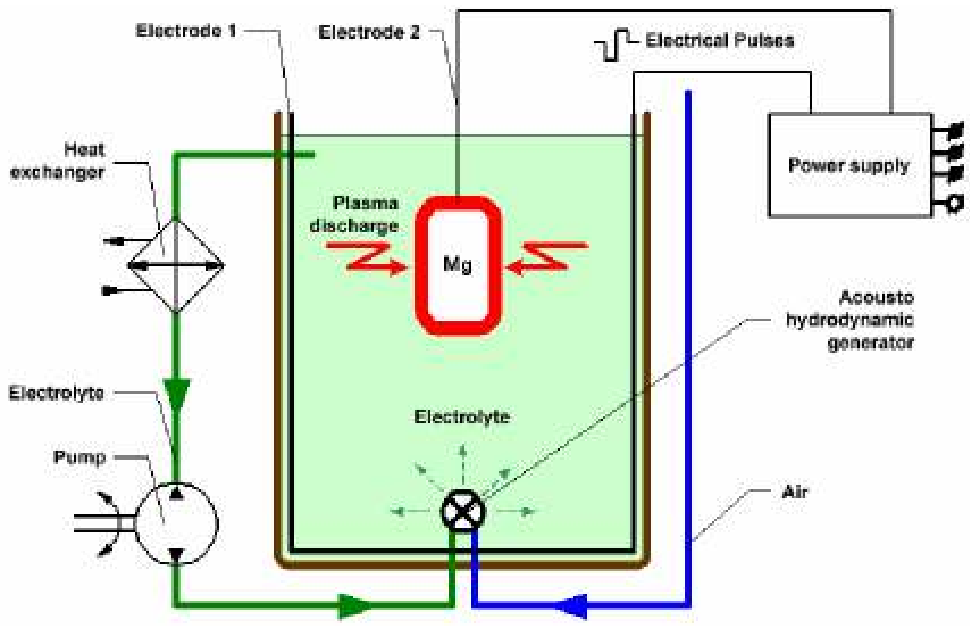


Figure 17 - Description of an anodizing process (44).

As shown in *figure 17, 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, a particular composition 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.
When AZ91 is treated, the typical structure of the formed film is shown in *figure 18 &19*

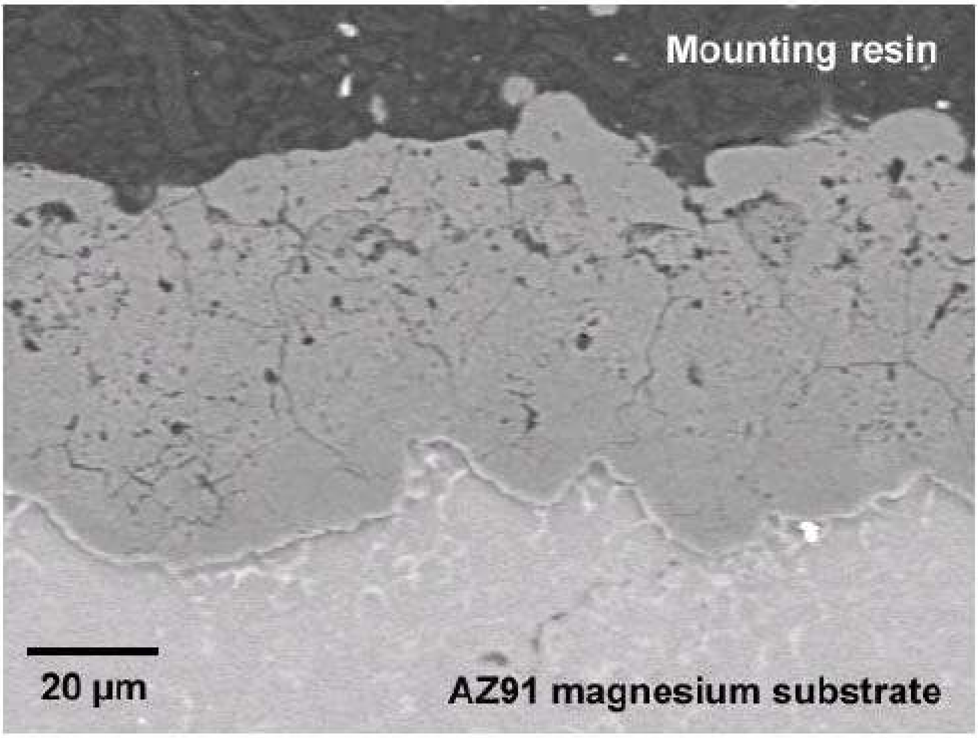


Figure 18 – Back scattered SEM micrograph of a polished cross-section through a 60 µm thick Keronite-type coating on an AZ91 magnesium alloy substrate. (45)

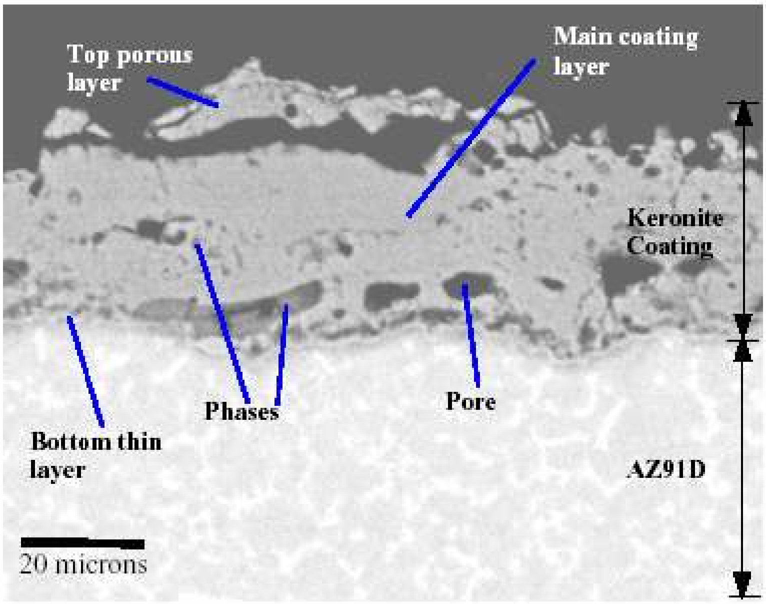


Figure 19 – Cross section SEM image of as-deposited 35µm Keronite coating on die cast AZ91 (46)

With Keronite process applied on AZ91 alloy the formed film is claimed to be, essentially, composed by $MgAl_2O_4$ and a minor content of SiO_2 and SiP_2 related to the anions usually present in the solution. With different alloys or different processes applied different and more complex chemical salts are formed on the magnesium surface.

When a spark effect occurs the layer structure is as in *figure 19* as schematically sketched in *figure 20 (42)*

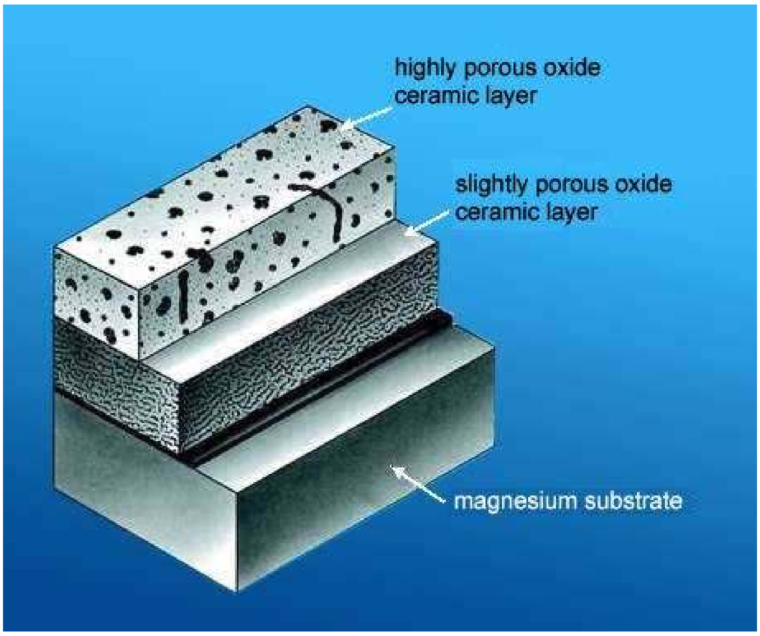


Figure 20 – Sketch of an anodic coat on magnesium (42)

In practice, the outer part of the layer (2-3 micron) is very coarse, uneven and friable; the inner layer is more compact and hard. For some mechanical applications where a strong hardness is required, the external coarse part of the film is eliminated by abrasion.

On the contrary, being more porous, the external layer can be a good base for a subsequent painting step.

This type of process is frequently named “micro-arc” anodising (MAO) or plasma electronic oxidation (PEO) and is quite common even applied on aluminium alloys when a very hard coat is requested *(47).*

The sparks formation is quite impressive as shown in *figure 21.*

The photo shows a “light effect” produced in the anodising solution caused by the parks between anode and cathode. The amount of energy formed and partly “wasted” in these conditions is significant. Part of the current, in fact; is lost as heat that increases the temperature of the tank (that a suitable chiller maintains in the correct range.

Figure 21 – Micro-arc or spark anodising process performed on Italfinish pilot plant

2.2 – Description of our process.

When we were asked to set up an anodising process for magnesium alloys the main issues concerning it were:

- it should be simple,
- it should be environmental friend and low energy consumption,
- it should be suitable for different magnesium alloys.
- It should give a pleasant aesthetic finish because, probably, some pieces could remain as-prepared without any additional post-treatment or covering top coat.
- In practice, it should be "low cost" because to be applied to mass production items, where the finishing cost should not be a significant part of the total cost.

When we started to find some basic data about the pre-treatments *before anodising,* we found a lot of data *(48)* but essentially all the methods include

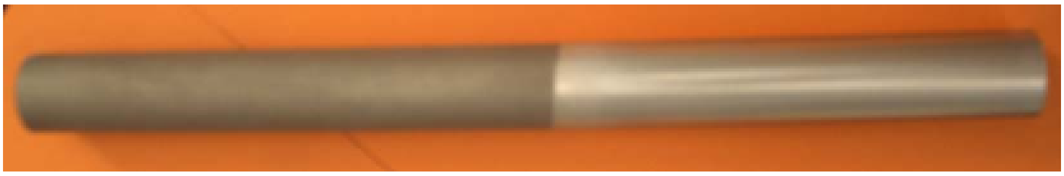
- an alkaline degreasing,
- An acid etching or activation using different acids, some of them really harmful like chromic, hydrofluoric or nitric.

For sure this type of chemicals were out of our a.m. basic statements even when we decide to use more friendly acids, the results were surprising and controversial.
Even comparing similar and very simple alloys like AZ91 or AZ31 we have some surprising results:

1- Some parts, essentially extrusions; after acid etching appeared silvery and "bleached".
2- Some other more frequently on cast parts (but not always) formed a thick black patina that partly could remain even after our anodising step.

The reason of the different behaviour is related production technology, type of "protective" gas used and the injection and /or cooling system especially on cast part.

We were widely informed about the "SF_6 Reduction Partnership" proposed by US Environment Protection Agency EPA and the conferences yearly organised *(49),* but our main task was to *avoid the problem, because we were acting as "job" anodizes not as expert of magnesium die casting or extrusion.*
Figures 22 & 23 are examples of the mentioned problem.



(a)

(b)
Figure 22 – Examples of magnesium extrusion partly etched in acid solution for 15 second (right part) (22)


(a) *(b)*
Figure 23 – The same die cast before and after acid etching (22)

The sole way to avoid the problem was to skip the acid step and any pre-treatment in general.

To do so, we had only one way: to perform the cleaning and subsequent step with an electrolytic step.
We contacted an important Italian manufacturer named Elca *(50)* asking to prepare a special current supplier fitted with a PLC to manage type and duration of the supplied current / voltage.

The prototype manufactured for us was successful and the machine is in production and some pieces already sold. The feature is available in the mentioned website.

Figure 24 – Current supply and its special control board (49)

A correct combination of type of current and time gave a positive result even because when the magnesium items had no so good dye casting process the aspect was better if processed *without any preliminary step.* When the material is originally good, we had exactly the same result *with or without* a preliminary acid dipping.

Table 5 represents a summary of *SweetMag*™ process

Table 5 - SweetMag™ process

Parameter	Description	Notes
Type of finishing	• Stand-alone anodizing • Anodising + adsorption colour • Anodising + powder coating • Anodizing + wet paint • Anodising + ED paint	**1, 2, 3**
Type of metal	- Magnesium (any alloy) - Aluminium (any alloy including high-silicon ones) - Titanium (any alloy but the aesthetic result depends on the alloy). This type of finishing can be considered according to the American MIL Specs.	**4**
Type of treatment	Electrochemical, operated in the same chemical solution, by means a special electrical supply managed PLC	
Type of pre-treatment	Not necessary in some cases detrimental	**5**
Type of post-treatment	According to the final application: • Not visible sealing • Powder coating • Wet paint • ED paint Any paint coat can be considered as a base coat, to which the final customer can add his final top coat, according to his real need. Top coats can be applied even by the final user of the items.	
Type of plant	Full automatic, including wastewater recycling and fume suction and recycling.	**6**
Chemical solution (electrolyte)	Diluted alkaline solution, free from chromates, borates and fluorides. The solution is long-life.	
Maintenance of the solution	• Replenishing the consumption by addition according to specific, simple chemical analysis. • By filtration	
Temperature	25 ± 5 °C (preferred)	**7**
Phases of the electrolytic process	• Cleaning and activation step. This proprietary step is necessary to eliminate any grease, oil or friable part from the surface and making it reactive to the subsequent process. • Anodising	
Current density (in the anodising step)	2.0 A/dm^2	**8**
Voltage (in anodising for 20 µm layer)	• Below 300 (maximum) • Below 180 (average)	**9**
Total cycle time (for 20 microns)	18 minutes	**10**

Notes	1. Thickness of the anodic layer ranging from 5 to 25 microns, according to the customer's request or final application. Thicker layer has no technical meaning. 2. The anodic layer can be coloured by adsorption, if using special organic dyestuffs, but the aesthetic effect is not comparable with same treatment on aluminium 3. The adhesion of any subsequent paint is excellent, but the behaviour depends on the type of paint. Multi-layer paint is possible by applying a correct procedure. 4. Different metals can be joined together. 5. In case of superficial defects or problems on cast pieces, a soft deburring or basting step is suggested. In case of blasting, it's advisable to avoid any metallic or metal containing media, because able to cause corrosion pitting during storage. 6. The plant can be organised as a "closed boxes" system when manpower is used only for racking and un-racking. A proprietary close loop system can be used to recycle waste and fume 7. The temperature of the solution influences the voltage necessary to maintain the preset current, and should be chosen according to the final application. The influence of the temperature on the layer characteristics is not so evident. 8. This value was decided for all the alloys and coating thickness. The process can operate even at lower current density, because the formed layer is conductive and no high current density is necessary to "perforate" the formed layer and maintain the conductivity. No spark formation. 9. The maximum and average voltage depends: • Final thickness of the layer • Alloy • Temperature of the solution 10. All the operational parameters have been chosen to produce 3 loads/hour with 20 µm layer. Due to the type of process, thickness and time are not *strictly* proportional.

2.3 - SweetMag™ in practice (magnesium)

This section is a photographic documentation of some application of our technology.

§ 1 – Example of industrial production

The request was:

- 15 µm anodic coat
- Powder top coat (the powder was supplied by the customer)

The result is shown in *figures 25 – 30*

Figure 25 – Multi-purpose pilot line in Italfinish

Figure 26 – Packaged pieces arrive from the customer (22)

Figure 27 – Particular of the control board of the current supply almost at the end of the process. The full control board is shoe in figure 24.

Figure 28 – Anodised pieces ready to enter the powder coating booth, (on the left) and subsequently to the curing oven (on the top)

Figure 29 – The powder coated pieces after the curing oven (on the top)

Figure 30 – One of the pieces after powder coating and ready to package. The sample is same type of figure 23, and no evidence remained of the previous superficial problems.

§ 2 – Wheel
Cast magnesium wheels are common items. *Figure 31 - 33*

Figure 31 - Scooter wheel after anodising (similar item of figure 6) (22). The brown plastic tape has been used to cover a mild steel insert present in the sample we received.

Figure 32 – Scooter wheel after anodising and epoxy base coat by DuPont. The additional coats will be added by the final customer later.

Figure 33 – Motorcycle cast wheel after anodising and wet paint (by DuPont)

§ 3 – Forged parts (alloy ZK60)
ZK60 is a special alloy very difficult to treat. Anodising is the most reliable process

Figure 34 – Forged wheel-hub with no treatment.

Figure 35 – Forged wheel-hub after anodising and epoxy base coat

Figure 36 – Forged wheel part after anodising and ED paint (BASF)

§ 4 – Special finishings

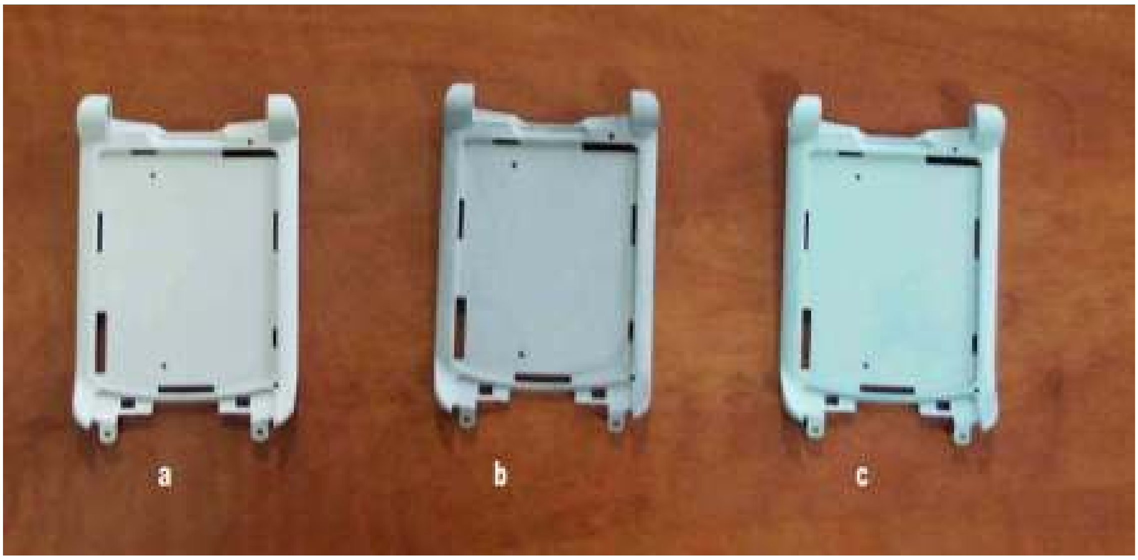


Figure 38 – Part of cell phone case: a) anodised only, b& c) coloured by dipping in organic dye stuffs. This type of finishing is requested by some producers (22)

Figure 39 – Part of cell phone case after anodising and powder coating (22)

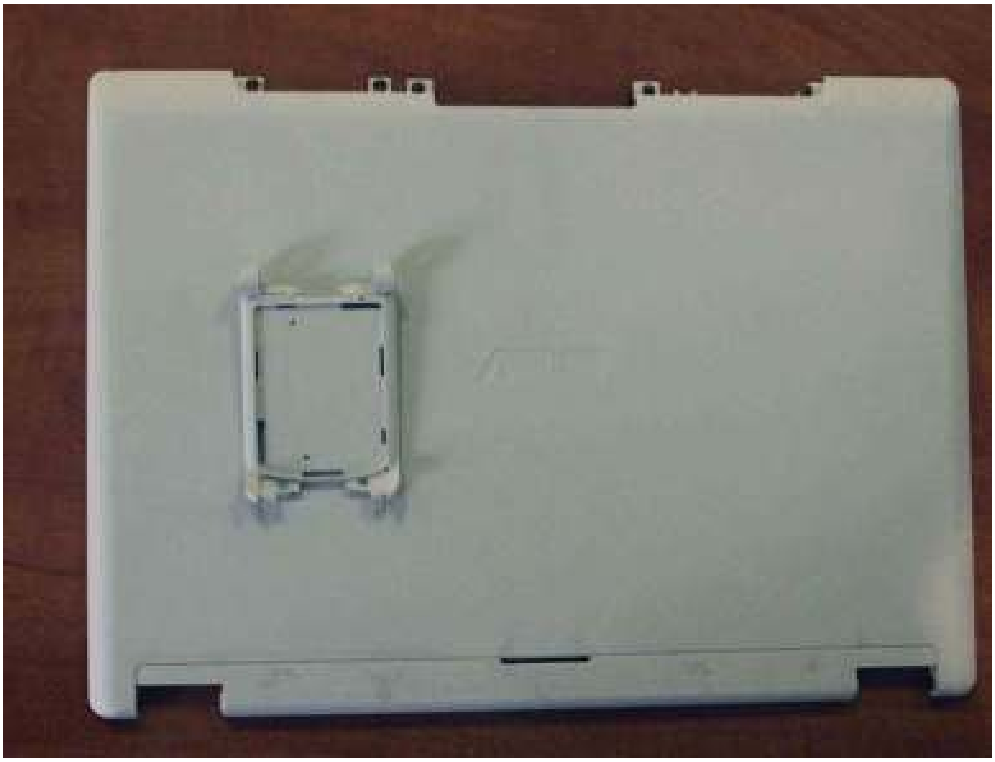


Figure 40 – Stand-alone anodising on cell phone and PC casing. The difference in aspect depends on the quality of casting (22)

Figure 41 – Special decorative finishing produces by sublimation on anodised magnesium. In this way any plain of fantasy coloration is possible. (Italfinish proprietary process)

2.4 - SweetMag™ in practice (aluminium)

The process shows certain validity when used on high silicon aluminium containing alloys, because able to produce a clear finishing even over 12% Si... The anodic layer doesn't show the blackish aspect, frequently with patina, typical of any sulphuric based anodising on that alloy, as shown in *figure 42.* This type of anodizing is an excellent pre-treatment to a subsequent paint because not forming any superficial patina. High silicon aluminium alloys, usually; give a not completely satisfactory result when painted after any conventional chemical conversion due to a scarce adhesion of the paint layer.

Figure 42 – AlSi12 die-cast alloy anodised aluminium

When the alkaline anodising is applied standard 6060 aluminium alloy the finishing appears opaque, as in *figure 43.* The formed layer has a significant covering effect able to mask even evident extrusion lines. This type of finishing produces some interest in automotive application.

Figure 43- Comparison of AA 6060 aluminium alloy after conventional and alkaline anodising

3 – The quality control of the finishing produces with SweetMag™

Note: Before any decision to start our production a long series of tests was specifically performed by Qualital Laboratory of Cameri (NO) on samples prepared by Italfinish (51)

A very serious problem we had to face with magnesium materials was that there are no "official" specification for quality control of magnesium finishing treatments.

There are some "internal specs." filed by the Companies or Groups of automotive or aeronautical field the "supplier" has to fulfil to be accepted in the "supplier's list".

All this is absolutely regular, but according our opinion it should be necessary to have some "basic" regulation to which everybody can refer.

For the tests described below, some tests are derived from those used for anodised and painted aluminium

The tests performed and the applied methods are as follows.

1) Measure of the thickness of the anodic layer with and without organic coating according to eddy current method (ISO 2360)
2) Measure of the thickness of the anodic layer with the micrographic method (ISO 1463)
3) Evaluation of the adhesion (UNI EN ISO 2409: 1996- cross etch).
4) Evaluation of the permeability of the coating film and the quality of the pre-treatment (pressure cooker test)
5) Test in humido-static cabinet (humidity 100%) (UNI 8744: 1986).
6) Neutral salt spray test (UNI ISO 9227:1993 – ASTM B 117)

Notes

1) *The "eddy" current method to measure the anodic coating on magnesium parts is "technically" correct because the thickness of a non conductive layer on a conductive base*

is checked, but, in practice, the high roughness of those surfaces make the measure not always accurate. The micrographic method gives a more precise result.

2) *Neutral salt spray test is used because the acidy of the acetic salt spray test commonly used for aluminium is not compatible with the strong reactivity of magnesium metal.*

Figures 44 – 50 are the photographic documentation of our tests...

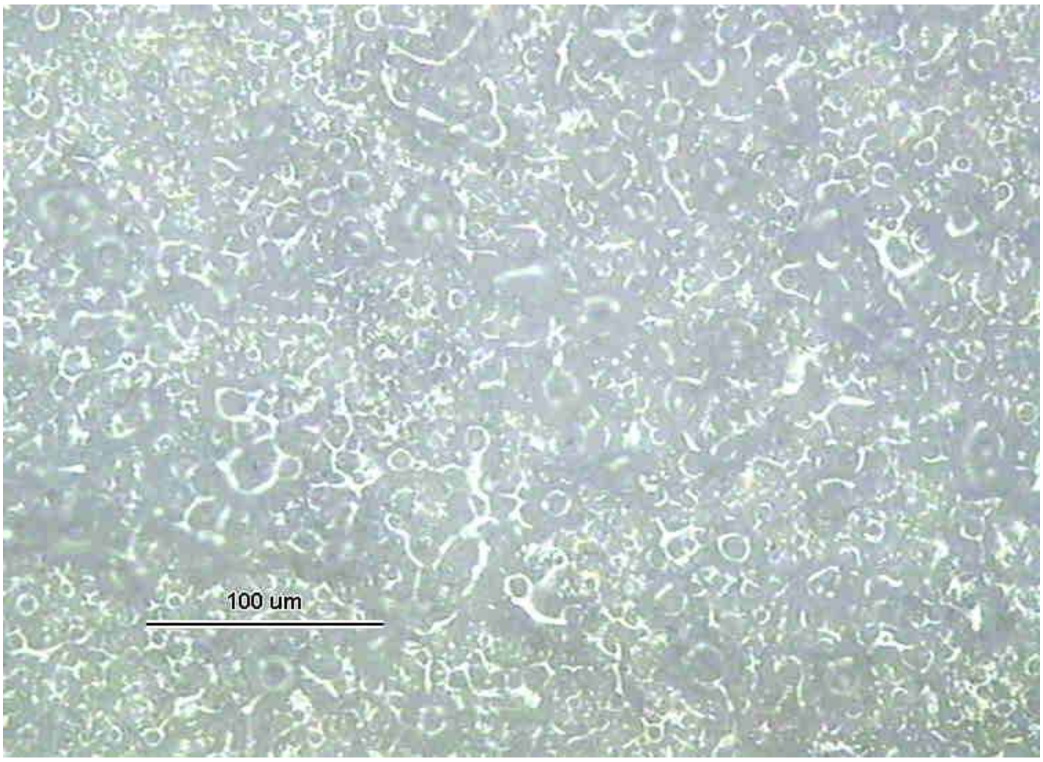


Figure 44 - AZ 31 anodised sample, magnification 200x (54)

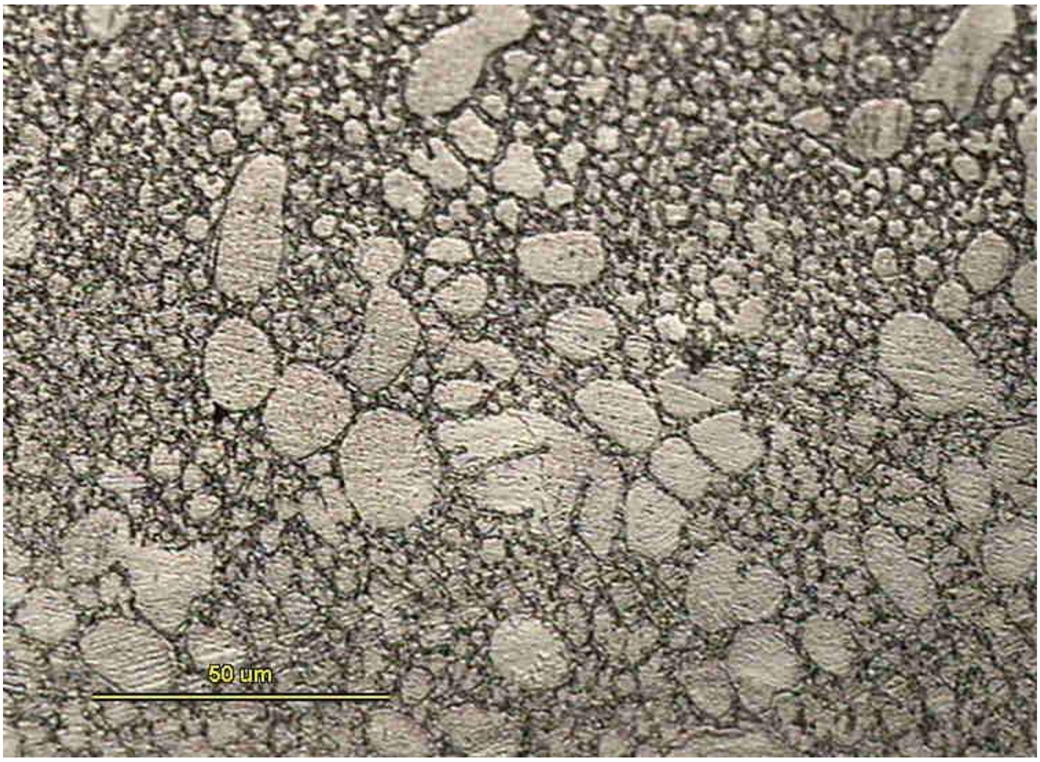


Figure 45 - AZ 31 anodised sample, cross section magnification 540x (51)

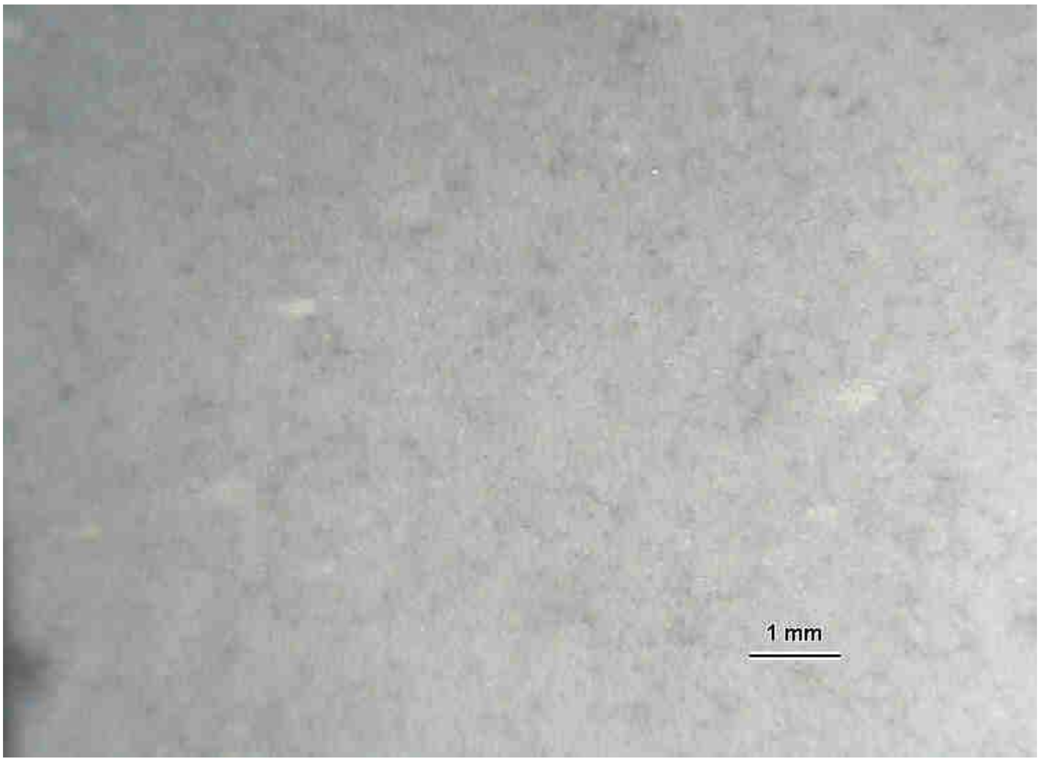


Figure 46 - AZ 31 anodised sample after 120 hours ASTM B 117 salt spray test (51).

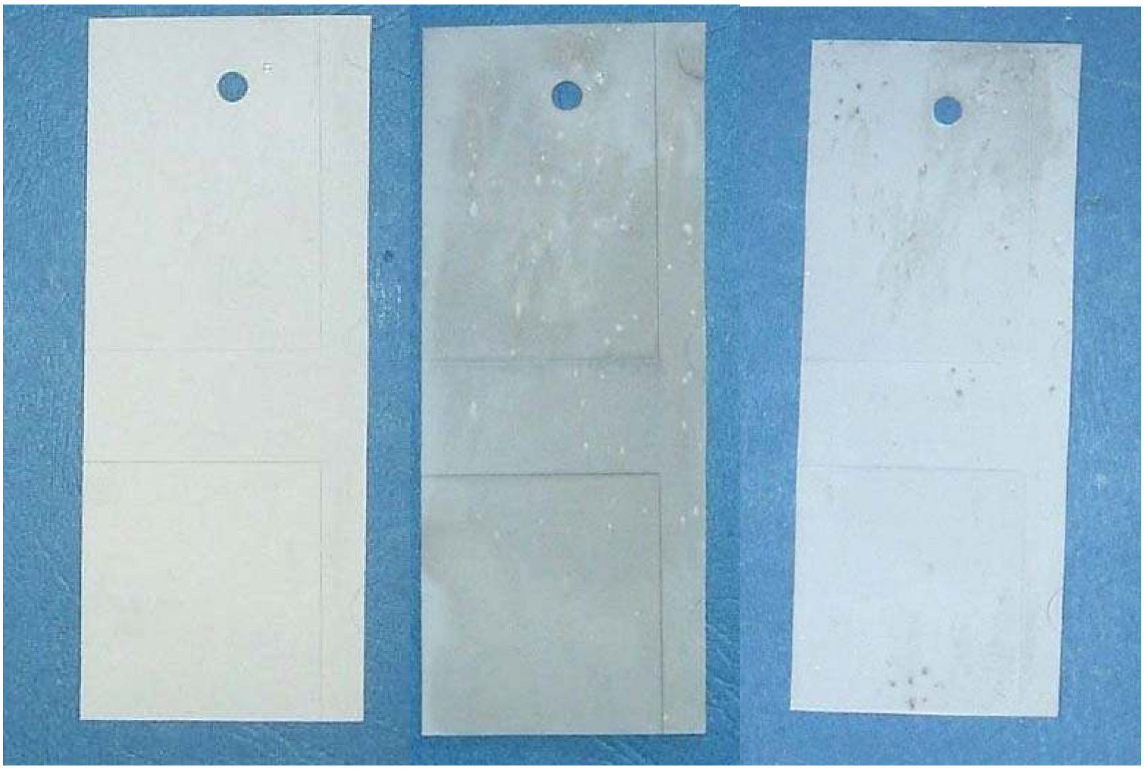


Figure 47 – Thixomolded AZ31 anodised samples, after 0, 100 e 503 hours ASTM B117 salt spray test (51)

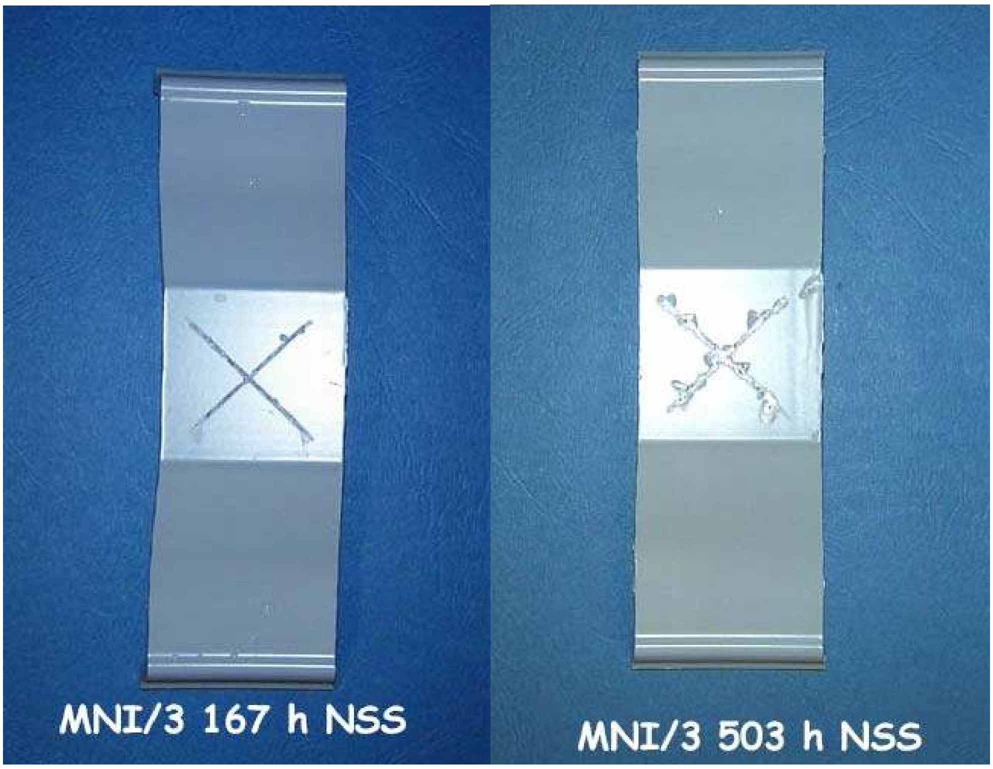


Figure 48- Forged ZK60 anodised samples + powder coating after 167 e 503 hours ASTM B117 salt spray test (51)

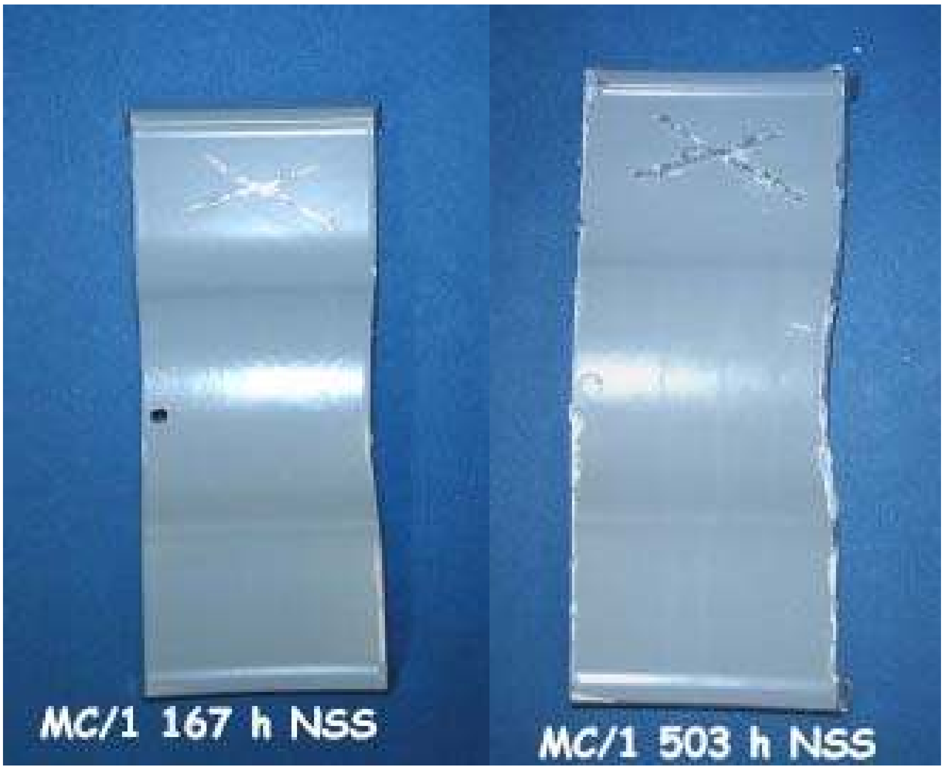


Figure 49 – Die cast AZ91 anodised samples + powder coating after 167 e 503 hours ASTM B117 salt spray test (51)

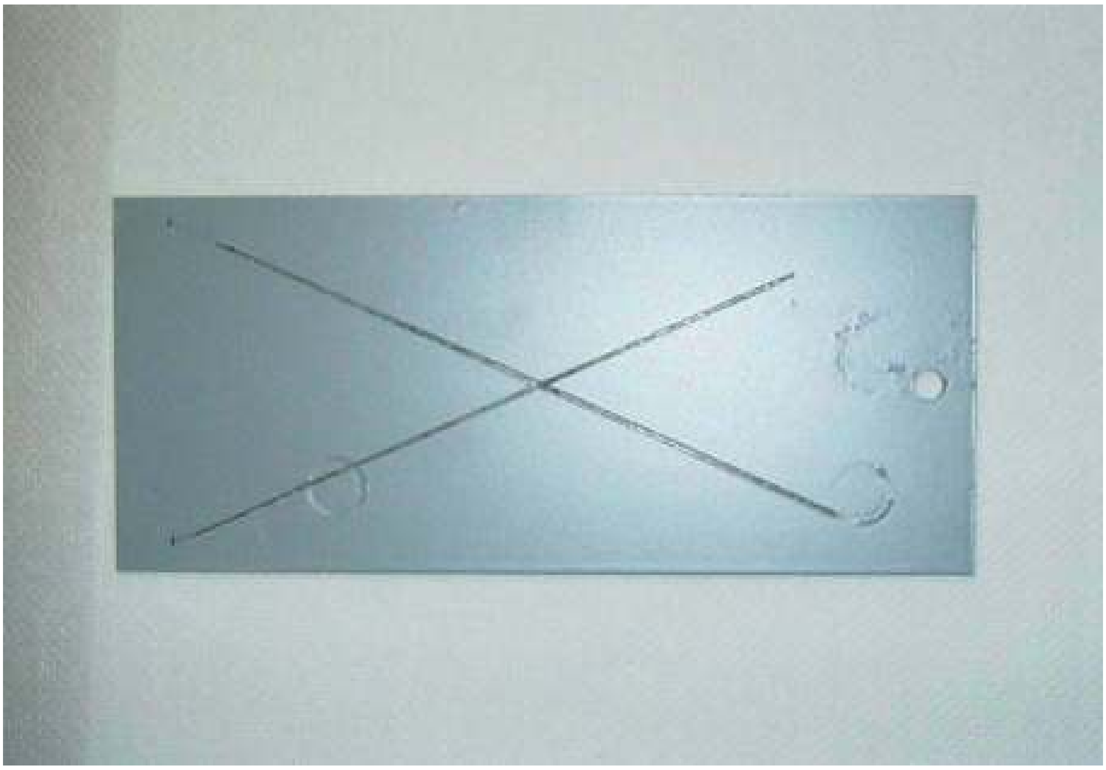


Figure 50 – Thixomolded AZ31 anodised sample + powder coating, after 1000 hours ASTM B117 salt spray test (51)

4 – Conclusions

The main task of the Authors was to set up a *simple, reliable, and low energy consumption* process essentially for magnesium and its alloy when a massive production was requested and the finishing cost should be not significant for the total cost of the item.

When a magnesium piece is an important mechanical part of a helicopter or a car, the cost of its finishing is easily "adsorbed" in the final cost of the vehicle. In some cases, special technical feature are requested to the finishing layer that can increase the cost of the treatment, but there is a wide share the market needing a good but cheap finishing. Let's mention a real practical example. Italfinish received some samples to be 20-micron anodised and colour black by painting. That was the specific request of the final customer (an "institutional" organisation of an important Country). We passed all the internals test of that organisation and we got the order, even because some local competitor failed. The main problem, now, was not the process, but the number of pieces: 100,000 items per year formed by 7 parts each for a total of 700,000 pieces / year…

In those conditions the choices was obliged:

- To settle a local facility,
- To study a very simple technology for a full automatic process where the man's action was related only to racking and un-racking the pieces. For that application an automatic racking is not easy and suitable because the parts can be damage.

The conclusion was:

- A full automatic plant
- A "simplified" treatment solution making it stable to the use and the time. The components are basic chemical that can be analysed and replenished when needed.
- A complete recovery and re-use of waste and fume with a proprietary technology.
- A long lasting racking system where the stripping was not necessary.
- ED coat for painting (and final customer appreciated this choice because in his original project).

This example should teach us the future market of magnesium finishing will be very wide with different expectances and requests concerning costs and environment.

Chemical conversions must be chrome free but with similar final quality.

Anodising must be low energy consumption, because when the production is high, even the needed total installed power can be a limit. Working at 10 A/dm^2 (and consequently 600 Volt), how claimed and applied by an industrial treatment, can be a serious problem if the production is 20 microns on 700,000 pieces per year. For sure 2.0 A/dm^2 (below 300 Volt) is simpler.

Let's finish this paper with an appeal to colleagues and technicians "let's help the producer to improve the surface quality of magnesium items and understand what can be possible or logical with magnesium parts".

In literature there is a wide documentation of the "mechanical" properties of magnesium, but no clear description of the finishing for magnesium parts. Magnesium is not aluminium and only in some physical properties (mechanics, melting point, etc…) the two metals are similar, but their chemistry is quite different. We should never forget it.

Magnesium is a baby growing fast, it's a technicians' task to protect and ensuring it a brilliant future!

5 – Acknowledgments

- To all the *master*s, never met personally, but from their patents we learned the basic of magnesium finishing. Considering some of their findings we feel like peasant growing potatoes…..instead of their … orchids!

- To Elca managers and technicians who supported us with their patience and experience to set up an electrical supply suitable to our specific needs and request.
- To Dr. Rossella Barbato (Qualital) who performed the quality tests and related photos exposed in **chapter 3,** with patience and professionalism.
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