THE ENAMELLING OF ALUMINIUM WITH A HIGH CONTENT OF MAGNESIUM

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Introduction

To plan and to choose an enamelling aluminium alloy it is necessary also to consider the physical properties that the alloy has to possess, taking into consideration the application to which it will be destined. For example:

- Resistance to the thermal shocks,
- Mechanical resistance,
- Deformation resistance,
- Resistance to fatigue strength
- Good enamelling properties

The matured experience, in aluminium alloy enamelling is relatively short and very limited in comparison to other metallic materials used for enamelling.

The developments are few which have been seen over the last decades, we think however that there are ample margin of growth to allow the use of the aluminium in the development of fabrication technologies which are today only the dominion of ferrous materials.

The work and study, until now developed in collaboration between enamels manufacturing, aluminium producers and of the final customers, have given a positive impulse to the knowledge of the materials and the understanding of their specific performances based on the final projected application.

In the last years, there have been produced and utilized some new suitable aluminium alloys for enamelling, with some dedicated enamels, for instance the alloy 4006, predominantly used in the production of the enamelled saucepans, or the enamelled iron-base-plates, but surely it is possible to do more.

Following we summarise the arguments, the works and the experiences matured in the last three years which have shown to us, how some aluminium alloys of recent realization, with a high content of magnesium, which possess important and positive physical characteristics, and result at the same time economical, and can be enamelled as the alloys normally in use.

Matters considered:

1) Fusion-temperature of the aluminium alloy
2) Influence of the contained chemical elements in the aluminium alloy
3) Influence of the aluminium surface
4) Tests of enamel adherence
5) The enamel
6) Theoretical aspects of the interface adherence between aluminium and enamel
7) Enamelling of aluminium alloy with a high content of magnesium

1) Fusion-temperature of the aluminium alloy

To be enamel an aluminium alloy it must first of all be resistant to the firing temperature of enamel which results approx. 540/560 °C. Different aluminium alloys have some eutectics that melt near to this temperature.

The alloy 1050, with min. 99.5 % Al, has a fusion range between 645 – 658 °C

For the alloy 3003 the fusion range is between 643 – 654 °C

For the alloy 4006 the fusion temperature is 608 °C

The fundamental characteristic of the aluminium alloys are the diminished mechanical characteristics after the thermal treatment, considering that the temperature of recrystallization results around 320 - 360 °C, it would consequently have materials, with low mechanical values, after the firing of enamelling.
2) Influence of the contained chemical elements in the aluminium alloy

An aluminium alloy is defined “adapt for enamelling” when a reaction of adherence happens to the interface between enamel – aluminium, and the enamels it results chemically bonded to the aluminium surface. Further more the surface of the enamel has to be without defects. Some elements and chemical compounds contained in the aluminium alloys have a notable influence on the adherence among aluminium / enamel.

The alloy 4006 mainly used in the manufacture of enameled pots and sauce-pans is an aluminium alloy with a silicon content of 1% and practically without magnesium (max 100 ppm). The alloy 4006 after the firing for enamelling for a very short time, followed by rapid cooling which causes a slight effect of solubilization and a temper-effect, which is sufficient to harden the metal.

The alloy 4006 shows a particular characteristic to temper slightly and to contain elements like silicon that favours the enamelling and the adherence of aluminium to the enamel. This alloy, after enamelling, unlike the other aluminium alloys, maintains its own mechanical characteristics after the thermal treatment at 560 °C, during the enamelling.

It has been observed on several occasions that as the content of the magnesium, in the alloy 4006 or 3003 and the 8006, also at low concentration, induces a worsening of the adherence between enamel and aluminum. When the magnesium overcomes a certain concentration, and even if in some aluminium alloys, it is contained as impurity, it does disturb the adherence between enamel and the aluminium support.

Which whilst it is important to underline that the alloy 6082 contains between the 0.6 and 1.2 % of Mg and 0.7-1.3 % of Si, otherwise the adherence between enamel / aluminium, is not upset by the presence of the magnesium.

The probable explanation is due to the formation of the compound Mg2Si (silicide of magnesium), the magnesium being tied to another element (Si), forms an inactive mixture in the matrix of the alloy.

The magnesium is a very important element in the aluminium alloy, it is added (also in small percentages) to increase the mechanical characteristics, or/and the resistance to the salt water corrosion, for the anodic oxidation, etc.

The lead and bismuth and all the elements that do act a low-fusion component in a matrix have a negative effect because they substantially disturb the adherence. And it was observed that the presence of lead or bismuth in some aluminium alloys, even in standard quantity as indicated below, and also at the same time in presence of the chromium and copper (in relevant quantities), the adherence was reduced.

The following table shows (to experimental title) which different elements influence in the adherence on enameled aluminium.
It is interesting to understand better the influence that some containing elements contemporarily present, in comparison to others and in certain quantities, reduce sensitively the adherence between the aluminium and the enamel, or in opposite cases, where they favour the bonding.

We know that the chromium, manganese and magnesium, are elements which further increase the mechanical properties of the aluminium alloy, they also result as important modifiers of the crystalline grain (they maintain a smaller dimension).

But we have also ascertained that the adherence enamel / aluminium results strongly influenced by the dimension of the crystalline grain.

The projected photo demonstrates this influence.

We have in fact observed on the same enamelled sauce-pan that on some parts were no adherence, whilst on other parts the adherence enamel / aluminium was good because the crystalline grain was larger.

Following the analyses of these samples we noticed that in the zones with large crystalline grains (zones of deformation with critical tempering and secondary recrystallization) the adherence was good where the grains resulted very small (bottom of the sauce-pan) the adherence was negative.

The cause of poor adherence of the enamel on the aluminium frying-pan was due to primarily excessive content of lead and bismuth in the aluminium alloy, whilst it is important to indicate the structure of large grains has cancelled the effect of non adherence due to the presence of the described elements.

An analogue problem was seen on the enamelled iron-plates.

It will be important to continue some studies of the enamelled - alloy to discover which type of elements, or which kind of structure favours or reduces the adhesion of the enamel onto the aluminium alloy.

3) Influence of aluminium surface. Residual

The chemical pre-treatment covers a notable importance in the mechanism of the adhesion between enamels and aluminium support. A good cleaning of the manufactured article, before applying enamel, is one of the most important stages of the complete process. We know for example, how some organic or alkaline residues, can risk the final result. We should remember the effect of the chemical pre-treatment, in practice the light chemical attack on the surface of the manufactured article with the purpose to increase the micro roughness on the aluminium surface.

At the same time the mechanical adherence will be improved. We are certain that a specific pretreatment can improve the adherence on the alloy considered difficult to be enamelled.

The above panel shows the aluminium support and the different substrates before the pretreatment.

A decisive factor to get a good adhesion between aluminium and enamel is the type of surface preparation that has been chosen.

The best known cycle for the preparation foresees:

1. Degreasing, with the purpose to eliminate the oils and fats on the surface without
1. Degreasing, with the purpose to eliminate the oils and fats on the surface without affecting the layer of oxide.
2. Pickling (mechanical or chemical), to remove a light surface-layer of metal, obtaining a micro roughness to favour the adhesion.
3. Chemical conversion (chromatisation or phosphate-chromatisation), to modify the nature of the oxides on the surface.
4. Anodization, completed by the deposition of a primer for the purpose to improve the adhesion.

4) Tests of enamel adherence
The official test used today is based on the attack with antimony 3-chloride (1% for 20 hours). Therefore, the result is obtained after 20 hours. We all agree that in the modern industry, 20 hours of production, before having the certainty of good adherence, are exaggerated with the risk that an enormous quantity of pieces could have to be destroyed.

The WG3, Italian working-group of C.I.S.P., has studied and experimented a "quick answer method" which is able to give an answer of good or bad adherence within one hour. The method is simple: you have to precede the attack of antimony 3 chloride with an impact-test, the same used for enamelled articles in iron. The enamelled surface deforms and lengthens hair lining the enamel. The chemical attack of the Sb 3-chloride is therefore favoured and accelerated in a way to obtain a sure answer within 60 minutes.

See the projected photo.

The Italian manufacturer introduces this new test on an experimental base and the Italian WG3 is preparing an official standard.

5) The enamel
This is not the moment to examine the many matters that concern the aluminium enamel and its manufacture; nevertheless some important aspects which refer to the enamelling of aluminium with a high magnesium content are mentioned.

- How is it done?
The vitreous enamel used today for the aluminium enamelling is obtained by a frit of tender glass (silicon, sodium, potassium, titanium, calcium, and alumina). To allow the enamel to melt at temperatures approx. 600 °C, vanadium oxide is used for form a eutectic alloy that melts at this temperature.

- How is it manufactured?
Every producer uses additions of further elements which enter in the glass matrix favouring the adherence or the acid resistance, or they lower the point of fusion or to stain the frit. This type of frit provokes a strong reaction between the raw materials during the fusion process; it achieves an increase of volume of 2, 3 or 4 times in relation to the used temperatures. For this reason the fusion in a rotary furnace is recommended for a better maturation and refinement of the glass which can be obtained in the discontinuous furnace. This frit can be soluble in water at high temperature; therefore the cooling should be done...
In this context, it can be soluble in water at high temperature; therefore the cooling should be done with quenching cylinders and not directly in water.

- **Pre grinding**
  The pre-grinding has to be done in a dry mill, because of its solubility and with all the necessary precautions to its particular nature.

- **How to improve the adherence**
  Test with frits of different degrees of fluidity on the alloy 3105, which was considered not suitable for enamelling because of the Mg-content, have shown that:
  a) As more the enamel is fusible, the better is the adherence, we think because of an improved wetting power.
  b) If the enamel is left transparent it loses the adherence completely.
  c) The mill addition of some oxides and their compounds (from 1 to 10 %), increases the adherence enormously.
  d) The mixture between soft and hard frits, with the addition of an opportune mixture of oxides will assure us the possibility to enamel the alloy 3105.

6) **Theoretical aspects of the interface adherence between aluminium and enamel**

The understanding of the mechanism that allows the adherence between the two materials would facilitate the development and the improvements both of the product: aluminium alloy and enamel.

The aluminium is a material with a crystalline structure, whose atoms are arranged in a cubic network with centred faces and with metallic bonds, while the enamel is a solidified glassy mass, with a solid structure of a non-crystalline type, in which prevails an ionic type bond.

The physical-chemical bond between these completely different materials develops it through a mechanism at different levels:

- **The first**, in which the metal is oxidizing of slightly, with the increase of the furnace temperature in the oxidant atmosphere of the firing furnace. The layer of aluminium oxide should grow according to the theory up to a thickness of approx. 150 – 250 angstrom (1 angstrom = 10 elevated -10m) to obtain best conditions for a bond with the enamelled layer, according to the ionic mechanism redox. (Later on we will verify the influence of the oxygen in the furnace atmosphere and the real growth of the oxide layer).

- **The second**, when the enamel is liquid and it wets the metallic surface, dissolving the present oxides which react with the oxides contained in the fused enamel.

- **The third**, during the few minutes of firing, the layer of aluminium oxide dissolves it completely in the fused liquid enamel. The base metal is attacked and corroded by the fused enamel which penetrates in the micro rough metal surface, achieving (after cooling) the mechanical adherence.

- **The fourth** is the fundamental mechanism of ionic exchange between e “heavy metals” of metal alloy with the silicates and oxides of the fused glass. The presence of some more noble oxides, dissolved in the enamel or in the metal, offers the power to favour the ionic exchange. In this way forms an interface composite, which bonds aluminium and enamel makes them inseparable.

As a good adherence is the most important indication of "good enamelling", we summarize the points up to now listed, the parameters that influence the adherence and the phenomenon that happen during the firing:

:: Chemical composition and the reactivity of the aluminium surface
:: Pre-treatment of the articles to be enamelled
:: Quality and quantity of the oxide layer which is formed on the aluminium alloy
:: Firing temperature
:: Furnace atmosphere
:: Firing time
:: Quality and quantity of the oxides which determine the adherence of the enamel
:: Quality and quantity of the oxides and compound witch are added to the mill
:: Ability to wetten / fluidity / viscosity, of the liquid enamel / surface tension
:: Presence of the elements which determine the growth of the oxide
:: The thermal expansion of enamel
:: For the aluminium, the presence of crystalline grain

7) **Enamelling of aluminium alloys with a high content of magnesium**

**Choice of the alloy**

In accordance with the aluminium producer, we identified an alloy, the 3105 which results to be produced in big quantities. This alloy contains magnesium (0.5 %) too much for to be considered suitable for enamelling. At the same time, this alloy possesses a complete range of positive characteristics physical-chemical-mechanical, furthermore the important consideration that is produced in big quantities of "scrap" and secondary aluminium, and is therefore very interesting under the economic aspect.

Some producers of pots, who use the 3105 for the items not to be enamelled, would have also the economic advantage to reduce the warehouse-stock by using a single alloy.

**Variations in the alloy by the producer**

The aluminium producer has the assignment to identify and add to the alloy, during the fusion process, the metallic elements that have the ability to combine themselves with the magnesium to, in presence as free oxide, at the interface aluminium – enamel, as for example the silicon which binds the magnesium forming the silicide of magnesium. These additions have to be such, for quantity and typology not to risk the principal characteristics of the alloy.

To respect the "privacy of the producer", we don’t list what elements have to be added, we indicate only that the elements are not particular (strange) but p.p.m of metals, commonly used in the trade.

**Variations of enamel**

First we have developed a frit harder and a softer version in comparison to the standards of production, adding some oxides able to react positively with the magnesium. With a mixture...
of these frits, we created an "enamel-test", to verify in practice that the concepts, until now discussed, corresponds in reality. The first interesting discovery was that the enamel kept transparent (without pigments), has practically no adherence. Under this condition, we have verified which type of elements could be added to favour the adherence.

Another interesting discovery was to ascertain that every oxide or compound we used, as well as the colouring oxides, improved in any case the adherence.

Certainly only few elements have the ability to increase the adherence but contemporarily not to stain the enamel, not to decrease the acid resistance, not to provoke superficial defects and not to harden the enamel.

For not depriving you the satisfaction to discover it yourselves, we do not mention which is the best addition; we indicate only that it is a mixture of products you can find normally in commerce. For this reason the new aluminium-enamel doesn't have superior costs than the enamels normally purchased.

**Industrial tests**

After the necessary verifications in laboratory and some tests with limited quantities by small producers of holloware, we organized a test on industrial level referred to thousands of items by one of the most important producers of holloware in Italy.

The result was excellent under normal working conditions for this typology of pieces, with a normal pre-treatment and an only one application with and one firing:

:: Glossy surface
:: Good development of the colour
:: Good adherence controlled with the standard method and the new "fast test"
:: Chemical resistance of enamel analogous to the enamels normally used

The only recorded obstacle was the necessity to modify the tolerances of joining, between holes and aluminium nails, because of the higher hardness of the alloy 3105. All these pieces have been sold after severe control.

This project is therefore concluded and is also ready to be used even for opposing the competition like "Chinese", that is becoming every stronger.

**Conclusion**

We have always known that the magnesium is an important element in the aluminium alloy but it does risk the adherence of the vitreous enamel, when its content is higher than max 100 ppm. If the magnesium is bonded to another element to form a compound, then it results practically inactive.

Furthermore we know that some aluminium alloys containing magnesium (or magnesium compound), have the tendency to modify the aluminium surface by roughening it because of an increase of the oxide layer on the surface.

We thought therefore that it is necessary to inhibit the negative effect of the magnesium adding stoichiometric quantity of another compatible element to bond it, for instance the silicon, to form the compound Mg$_2$Si (silicide of magnesium).

To get the desired result, after having understood what are the mechanisms that interact during the process of enamelling, it is necessary to modify in a substantial but not complicated way, in three directions:

a) With a new alloy formulation, obtained by adding a small quantity of suitable elements, in stoichiometrical equilibrium as described before. These elements are normally used in the trade. (For example the SiO$_2$ which bonds the MgO).

b) Modifying the frit by adding a small quantity of more noble oxides, but these are normally used by the experts in frit formulation.

c) Modifying the enamel with mill additions, always in small quantities of inert elements, oxides or their compounds, normally used by the expert in our section.

We apologise for not indicating with more precision the used products and their concentration because an existing patent request.

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**References**


