Nickel Free Room Temperature Seal: an innovative and ecological process

2015 ANODIZING CONFERENCE
San Diego, California

Prepared by: Marcello Rossi
Italtecnno Srl
Italy
ABSTRACT

One of the most common surface treatments on aluminium is anodizing. During the anodizing process there is the formation of an oxide layer called anodic layer that has a porous structure. The anodic pores must be sealed with a process called “sealing”.

The sealing of the anodic oxide is traditionally performed by means of hot sealing, medium temperature sealing, or cold sealing. The traditional hot and medium temperature sealing processes require high-energy expenditure, while the traditional cold sealing is a process based on nickel, which has a high degree of toxicity and is highly allergenic.

The new Nickel free cold seal technology has a patent pending and is already been submitted to Qualanod tests for Qualanod certification.

The new nickel-free cold sealing guarantees new features to anodizing which allow the application of anodic oxide also in areas that, until now, were not a prerogative of anodized aluminium.
INTRODUCTION

Procedure for protective sealing of anodic oxide and its alloys that confers resistance to aggressive alkaline agents without nickel salts.

This invention concerns a treatment method of the anodic oxide formed electrolytically on aluminium and its alloys, in order to confer to the material a satisfying resistance to outside corrosive agents, in particular the alkaline ones, superior to the resistance given by traditional sealing with demineralized water or nickel salt based.

The anodizing process of aluminium and its alloys, produces the formation of an oxide layer which has an excellent adherence to the metal, high flexibility and hardness but, because of the porous structure, it is characterized by weak resistance to outside chemical agents.

From this derives the industrial practice of the treatment called sealing, due to which the oxide gains a satisfying resistance to external agents, that allow the obtained material to be used for various and also severe applications.

Different sealing methods have evolved from the beginning of the practice of anodic oxidation on aluminium and its alloys. Most of them consist in the immersion of the anodized part in demineralized water or in aqueous solutions containing nickel salts or cobalt at a temperature near 100°C for a time that varies from 30 minutes to 1 hour, according to the oxide thickness.

It is a generally accepted opinion that the sealing process causes the transformation of the aluminium oxide in Boehmite; this transformation occurs above 80°C and its efficiency increases as the temperature increases.

There are different theories on sealing. Initially it was believed that the sealing process caused the closure of the pores, now the theory is that there is a more complex action that includes the partial tightening of the pores and the formation of an impermeable gel at the base of the pores. The action of the nickel salts, the cobalt and of other metals is explained with the tendency that they have to precipitate as hydroxides according to the pH of the used solution.

Even though the process gives satisfying results, it does not represent the best solution; this sealing, even if carried out in the best conditions, does not confer to the material the resistance to different corrosive environments, even mild ones, in particular of the alkaline type, such as lime plaster and water-soluble dyes. The resistance to alkaline aggressive
agents is very important because oxidized aluminium is largely used in the building and decorative automotive fields where, alkaline detergents are often used for cleaning. The process costs are high, as there is a considerable energy consumption to maintain the bath at nearly boiling temperature; the costs are also high in case the procedure is carried out with vapor, as it often happens. It is therefore natural that, for a long time now, studies have concentrated on developing anodic oxide treatment procedures that confer improved protective characteristics, with reduced costs.

**EXPERIMENTAL PART: THE NEW PROCESS**

Researches are mainly focused on the use of chemical composites that have anticorrosive “sealing” properties with molecular dimensions that allow them to enter the pore by capillarity and also to coat the pore walls. This research represents a further progress in the anodic oxide sealing technique. The procedure, object of this invention, is made of 2 phases: a first phase at room temperature in a solution that contains active principles and pH buffer components, then a second step at a temperature of 65°C in a solution containing other active principles and pH buffer components. pH, time and concentrations are critical and of great importance in particular intervals as shown in the examples. The ion fluorides contained in the first “bath” activate the following reaction:

$$6F + Al(OH)_3 \rightarrow AlF_6^{3-} + 3OH^-$$

The alkalinization in proximity of the oxide pore determines a pH increase with consequent pore impregnation, which constitutes the first sealing phase. The second phase is necessary to complete the oxide pore filling process and the consequent complete anticorrosive protection. Thanks to the total stability of the sealing bath components, the life of the bath is practically speaking unlimited: in order to obtain the best results for long periods of time, it is sufficient to carry out simple checks and to periodically reintegrate the bath. The checks are easy to carry out for those who are familiar with anodic oxidation. The pH is the first parameter that must be checked, its value must be maintained between 4.0 and 5.0 for the first step; pH adjustment is done by adding ammonia, if its value decreases below 4.0 or by adding acetic acid (or formic acid) if it increases above 5.0.
The second parameter that must be checked is the concentration of mineral salts: with use, the bath progressively suffers the loss of its components caused by the consumption of the products due to impregnation in the oxide pores and also because of the introduction of rinse water with the anodized parts that enter the bath and also due to solution dragging caused by the exiting pieces.

This progressive dilution interests equally all bath components, therefore it is sufficient to determine one of them in order to know what the right quantity is to carry out the reintegration and bring the bath back to the correct concentrations.

The reintegration can be carried out by adding the separate products or with a concentrated solution of the necessary products.

Here following are 2 examples, that are given only to illustrate the process and are not intended to limit the present invention. They illustrate the sealing method application for stabilizing the anodic oxide.

The immersion time of the anodized aluminium pieces in the sealing solutions vary for the first step from 10 to 22 minutes, while for the second step we suggest an immersion time between 15 and 30 minutes, in general we suggest 1 minute for each micron of anodic oxide thickness.

Example 1
A plate of aluminium alloy P-Al-Si-Mg (UNI 3569) with dimensions 6x12x0,2 cm has been degreased, pickled in caustic soda, neutralized in acid solution and rinsed in demineralized water, then it has been placed in an oxidizing bath in an 18% H2SO4 solution (temperature 20°C), anodized with continuous current at a density of 1,5 A/dm2 for 35'obtaining a deposit of approximately 15 microns. All the samples have been treated in an anodizing pilot line (Fig. 1).

Fig. 1 Anodizing pilot line
The protective sealing is carried out according to the following invention: after removing the plate from the bath, it is rinsed in demineralized water and immersed in the sealing bath (first step) which is maintained at a temperature of 22°C, pH 4.3, for 16 minutes.
Solution concentration: 50 g/l as Hardwall EHR1
After a 16 minute immersion, the plate is removed, rinsed in demineralized water and immersed in the second solution (second step) at a temperature of 65°C for 27 minutes, pH 8.45.
Solution concentration: 50 g/l as Hardwall EHR2
The aluminium plate is then removed, rinsed in demineralized water and it is ready for the standard sealing tests.

Schematic procedure (example 1):

1) Boron-free degreasing

MG 19 NB3 (Italtecno) 50 g/l
Temperature 65 °C
Dipping time 10 min.

2) Rinsing in running water

3) Neutralizing

Sulphuric acid 120 g/l
Neutron 187 C (Italtecno) 30 g/l
Dipping time 2 min.

4) Rinsing in demineralized water

5) Anodising

Sulphuric acid 215 g/l
Temperature 20 °C
Time 35 minutes
Thickness 15 µm

6) Rinsing in running water

7) Rinsing in demineralized water
8) First step (nickel free)
Harwall EHR 1 (Italtecno) 50.0 g/l (in demineralized water)
Temperature 22 °C
Dipping Time 16 minutes
pH 4.3

9) Rinsing in running water 90 seconds

10) Second step (nickel free)
Hardwall EHR 2 50 g/l (in demineralized water)
Temperature 65 °C
Dipping time 27 min
pH 8.45

11) Rinsing in demineralized water

Example 2:
An aluminium plate with the same characteristics described in example 1 and anodized at the same conditions of example 1, is washed in demineralized water and immersed in the protective sealing bath (first step) at a temperature of 21°C, pH 4.4, for 10 minutes.
Solution concentration: 53 g/l
After a 10 minute immersion, the plate is removed, rinsed in demineralized water and immersed in the second solution (second step) at a temperature of 66°C for 18 minutes, pH 8.24
Solution concentration: 55 g/l
The aluminium plate is then removed, rinsed in demineralized water and it is ready for the standard sealing tests.

Schematic procedure (example 2):

1) Boron-free degreasing
MG 19 NB3 (Italtecno) 50 g/l
Temperature 65 °C
Dipping time 10 min.

2) Rinsing in running water

3) Neutralizing
Sulphuric acid 120 g/l
Neutron 187 C (Italtecno) 30 g/l
Dipping time 2 min.
4) **Rinsing** in demineralized water

5) **Anodising**
   - Sulphuric acid: 215 g/l
   - Temperature: 20 °C
   - Time: 35 minutes
   - Thickness: 15 µm

6) **Rinsing** in running water

7) **Rinsing** in demineralized water

8) **First step (nickel free)**
   - Harwall EHR 1 (Italtecnno): 50.0 g/l (in demineralized water)
   - Temperature: 21 °C
   - Dipping Time: 10 minutes
   - pH: 4.4

9) **Rinsing** in running water: 90 seconds

10) **Second step (nickel free)**
    - Hardwall EHR 2: 53 g/l (in demineralized water)
    - Temperature: 66°C
    - Dipping time: 18 min
    - pH: 8.24

11) **Rinsing** in demineralized water

**Sealing tests**
Here following are the sealing tests and the considerations of the advantages of the new technology compared to our reference patent and to the state-of-the-art.

**Table 1**

<table>
<thead>
<tr>
<th>Sealing processes comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss according to ISO 3210 with pre-dip</td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>Hot sealing (MG SEAL TZ) *</td>
</tr>
<tr>
<td>Cold sealing with nickel (Hardwall ) *</td>
</tr>
<tr>
<td>Cold sealing without nickel (Hardwall EHR1 + Hardwall EHR2) *</td>
</tr>
</tbody>
</table>
**Table 2**

<table>
<thead>
<tr>
<th>Resistance to alkaline agents</th>
<th>pH 12.5</th>
<th>pH 13.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot sealing (MG SEAL TZ) *</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Cold sealing with nickel (Hardwall ) *</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Cold sealing without nickel (Hardwall EHR1 + Hardwall EHR2) *</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>0 = no attack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 = mild attack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 = medium attack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 = medium-heavy attack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 = strong attack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 = very strong attack</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Proprietary products and trademarks Italtecnio.
From the above tables and graphs it is evident that the performance of both acid and alkaline corrosion resistance of the new Nickel free cold seal process is better than conventional Nickel cold seal and hot seal processes.

A complete study including fluctuation of chemical and physical parameters, effect of contaminants, salt spray test, Kesternich test and outdoor exposure test is under final evaluation and preparation and will be subject of a scientific paper to be published in September 2015.

Qualanod certification is expected by October 2015.
CONCLUSIONS

As it is possible to see from the accelerated tests for acid and alkaline corrosion resistance, the new Nickel free technology offers a better sealing performance compared to hot water seal and cold seal containing Nickel; the high resistance to alkaline solutions (high pH) makes this technology also suitable for applications other than the architectural ones, for all those applications where some resistance to alkali is also required. In the specific cases of automotive application, different types of seals are suggested, like Superseal 2S and 3S especially designed for passing the very severe alkaline tests described in the standards of the car industries (usually each different car industry applies different standard).

The new Nickel free cold seal technology has a patent pending and is already been submitted to Qualanod tests for Qualanod certification.

This innovation opens new perspectives to anodizers all over the world, since from today it will be possible to have in the line an ecological cold seal (no heavy metal) with higher performance with an easy installation in existing lines: in case of substitution from hot seal, there will be no problem since usually the number of sealing tanks allows simple changes, substitution from conventional nickel cold seal means just to use the former cold seal tank for the first step and the former aging tank for the second step where same temperature is required.

References:

1. Italtecn0 Italian Patent n. 40070A/82 –
2. Italtecn0 US Patent n. 4,549,910/85
3. Italtecn0 European Patent 0101820/90