Weather Fast Adsorptive Dyeing of Anodized Aluminum for Outdoor Applications

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Colored anodized aluminum offers unique optical effects which can’t be achieved by any other coloring process. It provides perception of high value with an eye-catching optical impression. Often a powder coating is given preference, as the process of coloring anodized aluminum is believed to be rather complex.

This presentation will highlight the most important factors that have to be considered for a stable coloring process and it will provide a guideline to achieve long lasting dyeing in outdoor applications. It is of essence to determine conditions such as anodizing parameters, minimum oxide layer thickness, minimum dye content in the oxide layer, optimum dye penetration, contamination with foreign ions during dyeing and sealing, and last but not least the choice of the right dye. Years of practical experience provides proof for the suitability of this process for architectural and other outdoor applications if basic rules are respected.

Qualanod, an independent certification institute founded by ESTAL (European association for Surface Treatment on Aluminum) and EWAA (European Aluminum Association and European Anodizers Association), asks for following specifications for architectural outdoor applications:

![General Requirements for Architectural Applications (Qualanod)](image)

These specifications are valid for all architectural anodized surfaces whether they are dyed or not. Little information is given about coloring with adsorptive dyes.

I will attempt to close this gap with interesting and important information about factors which affect directly or indirectly the light- and weather fastness of adsorptive dyed aluminum.
Anodizing Process for Architectural applications

In principle the anodizing process for outdoor applications is the same as for normal decorative indoor applications.

While it can be acceptable for purely decorative applications to have larger tolerances in all areas apart from shade, for architectural there is the need for tighter specifications. This is obvious as in addition to the optical effect, the oxide coating has to fulfill the highest requirements of light, weather and corrosion stability during a time frame of decades.

Typical alloys used for architecture are AlMg 1-3 for rolled products and AlMgSi 0.5-1 for extrusion-molded parts. To color these alloys, they must be of anodizing quality thus avoiding visible surface irregularities.
It is of little need to mention that the first steps of the process, degreasing, cleaning, etching and desmutting, are prerequisites for obtaining satisfactory results in the following steps. Prior to anodizing, the aluminum parts must be free of fat, dirt and old oxide layers.

**Anodizing**

Anodizing itself is carried out according to the sulphuric acid direct current process. The main difference between a standard coating and a coating for exterior application is the thickness of the oxide layer. It must be at least 25µm in average and must not be below 20µm on a single spot.
Deviations from these specifications will have significant impact on the properties of the oxide layer.

An increase in the sulphuric acid content of the anodizing bath will increase dye uptake, but reduce mechanical and corrosion resistance.
Too high of an aluminum content can lead to an inhomogeneous oxide layer with visible inhomogeneity in the color after dyeing.

The addition of acids like oxalic acid should be avoided as they can inhibit dye uptake.

Lower current density will increase dye uptake, but reduce mechanical and corrosion stability.

Higher anodizing temperatures will also increase dye uptake, but reduce mechanical and corrosion stability. Local temperature differences due to poor agitation of the anodizing bath can lead to uneven dyeings.

Summarized, the “Standard Exterior Coating” conditions can be seen as the best compromise for all relevant parameters for outdoor applications e.g. corrosion stability, color stability and an economic process.

After anodizing, it is most important to rinse the anodized parts for several minutes in cold running tap water. The rinsing water must be cold, as higher temperatures can later cause undesirable effects in the sealing operation.

Ideally dyeing should take place shortly after anodizing. During storage, the aluminum oxide coating may lose some of its dye adsorption capacity.

Dyeing

Dyes for architectural applications

Currently, the dyeing of anodized coatings is done in an aqueous environment. The dyes must be water soluble, must be small enough to enter the narrow pores of the oxide coating and must have a high affinity for aluminum oxide. For the coloration of aluminum mono-azo, poly-azo, metal complex
azo and polycyclic dyes have proven suitable. Not only metal complex dyes, but some metal free azo dyes and polycyclic dyes like anthraquinone or phthalocyanine dyes can be used in architecture. All organic dyes are more or less sensitive to high energy radiation like UV. Mono and poly azo dyes do not achieve the high requirements for light fastness in outdoor applications. Only dyes which reach light fastness ratings of >9 according to ISO 2135 are recommended.

Light- and weather fastness of organic dyes is not only dependent upon the chemical structure of the dye. Additional factors such as oxide layer thickness and the quantity of dye adsorbed in the oxide layer are crucial. Although the color intensity prior to exposure can visually be the same, coloration of thick oxide films shows better light/weather fastness than thin films. This is demonstrated in the next slide.

Two panels are shown with different oxide coating thicknesses. Each was originally dyed with the same intensity e.g. black after 8 years outdoor weathering in Basel/Switzerland. It is clearly demonstrated that the color is completely faded in the thin film while the thick oxide coating is almost unchanged.

The best light fastness will be achieved when the oxide layer is saturated with dye.
This slide shows a series of different dyeings with a metal complexed orange at increasing dye levels. Clearly evident is the poor lightfastness of the lighter shades. For this reason, light colors are usually not possible.

In order to increase the number of shades, a combination dyeing can be carried out.

In this case, the aluminum is first dyed electrolytically with a tin salt followed by an adsorptive dyeing. The electrolytic dyeing can vary from light to dark shades, the adsorptive dye must always have a minimum dye deposition.
The blending of dyes must be avoided as the minimum dye deposit for each single dye can no longer be ensured nor can it be controlled.

The amount of dye which can be adsorbed by the oxide film and the speed of adsorption depends upon the chemical structure of the dye, dye bath temperature, pH and use of buffer.

This diagram shows the speed of adsorption for an orange and a red dye. While the red dye is adsorbed very quickly to the saturation point, the orange needs much more time. In the end, the oxide coating adsorbs much more of the orange dye. (Test conditions: 12µm oxide coating, dyeing at 60°C.)
Another factor with an impact on dye uptake is dyeing temperature. Usually the higher the dye bath temperature the higher and faster the dye uptake will proceed. However, high temperatures are not always advantageous. The dye may be preferably adsorbed only near the surface of the oxide layer.

For optimal light/weather fastness, the dye should penetrate the pore as deep as possible. For a given shade, pH and buffer this is highly dependent upon dyeing temperature and dyeing time. Sometimes a deeper penetration is achieved at lower temperatures and longer dyeing times.

**Dye Penetration vs Dyeing Temperature and Time**

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Dyed Penetration [μm]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C/45°</td>
<td>15</td>
</tr>
<tr>
<td>35°C/30°</td>
<td>14</td>
</tr>
<tr>
<td>50°C/20°</td>
<td>12</td>
</tr>
</tbody>
</table>
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**Dyeing pH and buffer**

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Oxide layer: 12 μm Perauman 101 (EN AW-5005)
Dyeing: 0.5 g/l 20 min. / 60°C
Sealing: 5 g/l Ni-salt 30 min. 98°C
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**pH and Buffer**

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>No Buffer</td>
</tr>
<tr>
<td>7.0</td>
<td>NH₄-acetate</td>
</tr>
<tr>
<td>5.6</td>
<td>Na-acetate</td>
</tr>
</tbody>
</table>
The pH and buffer are of utmost importance for the adsorptive dyeing. The wrong pH or a missing buffer, where necessary, can significantly reduce the dye uptake of the oxide film. Not every dye behaves in the same manner. The recommendations of the dye supplier must be observed. In slide 15, the behavior of a green metal complex dye is shown. This dye reacts very heavily when missing a buffer. In this case the type of buffer had no big impact, but for other dyes it has. As an example, some blue anthraquinone dyes can only be buffered with ammonium acetate. Other dyes may not need buffer at all. It is critical that the optimum dyeing conditions are selected so that the minimum dye uptake can be achieved.

**Sensitivity to foreign ions**

Rinsing of the aluminum parts should not be underestimated as the “drag-in” of ions from the anodizing bath into the dye bath can have a significant effect on the dyeing power of the dye bath. Ions such as phosphates, sulfates, silicates and aluminum can drastically reduce the dyeing power. This means that the intensity of a dyeing can be reduced even though the dye concentration in the bath and all other dyeing parameters are within specification. As long as dyeing power is only slightly reduced this can be compensated by the addition of more dye to the bath. Be aware that there is a point where this is not economical and the whole bath must be replaced. When the dyeing power, known as “activity” reaches a value of 85% the dye bath must be replaced. At this point there is no guarantee that the required dye quantity is adsorbed into the oxide layer.

The sensitivity to these ions is different from dye to dye and can be determined in the lab by preparing a series of dye baths with different specific ion additions. With each dye bath a test plate is dyed under exactly the same conditions. The color strength of the test plates is measured and compared to a test plate without contamination. The slide above shows an example of an orange metal complexed dye:
As can be seen in slide 16, the type of ions affects the “activity” of the dye with varying intensity. Very low amounts of phosphate, in this example already below 0.02g/l, bring the dye bath below the recommended minimum activity of 85%.

Water Quality

The quality of the water used for the dye bath is critical. Tap water can already contain many ions which can interfere with the dye. The picture below illustrates an example of a green metal complexed dye. The tap water for the preparation of the dye bath had a hardness of 11° dH (degrees German water hardness) which is approximately equivalent to 80 mg/l calcium content. The reduction of the dye uptake is obvious! Clearly, deionized water should be chosen for optimal dye results. This is also particularly true for the stability of the dye bath which can further reduce dyeing costs.

Sealing

After dyeing, sealing is essential to close the pores of the oxide film. The quality of the seal has significant impact on corrosion resistance and light and weather fastness of the colored surface. There are a number of different sealing methods available from hot water to cold sealing. It is common to use a 2 stage seal e.g. nickel salt sealing followed by hot water sealing. It is important that the sealing time is long enough to completely close all pores. For a pure hot nickel seal this is approximately 2-3 min./µm oxide film thickness at >96°C depending on the seal additives.

Surprisingly the seal quality not only depends on the sealing process used, but also on the type of dye. Slide 18 shows a comparison of a hot water, mid temperature nickel free, and nickel fluoride cold seals combined with two different mid temperature seals. A pure nickel seal is shown on the far right with varying dyes on the left.
For architecture, Qualanod specifies a maximum weight loss of 30mg/dm². As can be seen, dyes usually increase weight loss compared to the undyed aluminum coating. However, there can be huge differences in final results depending upon the specific dyes and the type of seal. In this comparison a hot water seal as well as a two step cold seal or hot nickel seal give the best results. A Mid temperature nickel free seal must be used with care.

Dye Bleeding

Another aspect when sealing dyed oxide coatings is the problem of dye bleed back into the sealing bath. Since aluminum dyes are water soluble, they can be dissolved again into the sealing bath as long as the pores are open. In this regard, a pure water seal is disadvantageous as this process is quite slow. Nickel salt seals and cold seals close the pores quickly and can prevent strong bleeding.

Sealing Inhibitors

Nickel seals are also much more tolerant to seal inhibitors than nickel free seals. The next slides clearly demonstrate the impact of some seal inhibitors in correlation to the sealing process used. Mass loss is shown according to ISO 3210 with a hot water, mid temperature water seal at two different concentrations and a hot nickel seal. The seal bath was either contaminated by silicate or phosphate. While a hot water seal and mid temperature water seal react very quickly to the contaminants, the nickel seal stays relatively stable over the test concentrations.
Sealing Inhibitors ($\text{SiO}_4^{4-}$)

![Graph](image1)

Sealing Inhibitors ($\text{PO}_4^{2-}$)

![Graph](image2)
Durability of Adsorptive Dyeings

The weather fastness of adsorptive colored aluminum depends, to a significant degree, upon the climate where the aluminum is exposed. Humidity, temperature and UV radiation differ around the globe. A sea climate, because of salt exposure, is more demanding than a continental climate. For this reason, it is not easy to predict the lifetime of a dyeing in the lab or to provide a general statement.

Accelerated lab tests can only give a general indication for the durability of the colored aluminum. Actual outdoor weathering tests should be carried out with the selected dyes. For example, the following slide shows a turquoise dye exposed for ten years at different sites around the world.
Summary

This presentation has shown that each single step in the anodizing and adsorptive coloring process has a significant impact on the resistance of the aluminum finish and hence on the suitability for outdoor architectural applications. All process steps must be carried out with utmost care. Particularly, rinsing steps should not be underestimated as impurities introduced can deteriorate the properties of the colored oxide coating. Tight controls on all baths will secure satisfactory results.

Adsorptive dyeing for architectural applications is well established several decades. Experience shows that long lasting and eye catching colored aluminum can be achieved when the process is understood and some basic rules are observed. Recent examples are shown in the following pictures.