New technologies for colour anodizing
Issues driving change

Energy
➢ Anodizing has the reputation of being energy-intensive
➢ Electrochemical oxidation
➢ Hot water sealing

Waste
➢ Etching can produce large quantities of waste

Appearance
➢ “Checkerboard” panels on buildings
➢ Metallurgical non-uniformities

Car wash fluids
➢ Anodized aluminium has insufficient resistance to high pH
Long life and recovery etches

Long life etch

➢ Rate of dissolution of metallic aluminium equals the rate of loss of solution aluminium by drag-out into the rinse
➢ Aluminium sequestrant to keep aluminium in solution, eg sodium gluconate
➢ High aluminium concentration in solution gives the very matt appearance required by the European market
➢ High levels of waste sludge from etch rinse.

Recovery etch

➢ Precipitation of aluminium hydroxide by seeding and temperature modulation
➢ No additives in etch solution because crystallizer would remove them
➢ Low aluminium concentration means that the finish can be insufficiently matt for the European market
➢ Aluminium hydroxide by-product that can sometimes be sold.
Shot or sand blasting

Reduce the need for chemical etching

Blasting with steel shot or sand in compressed air

➢ stainless not mild steel, otherwise rust or corrosion
➢ cleans off staining, corrosion products
➢ removes the surface features, eg die lines, pick-up, weld lines, etc
➢ requires subsequent brief alkaline-etch to achieve satin finish

Finer abrasives such as alumina or glass beads in air or water

➢ uniform cleanliness and fine finish
➢ media consumption of brittle materials can be high – high costs

Shot blasting machine and effect on surface appearance
North American anodizers are using acid etching in solutions based on ammonium bifluoride (NH₄HF₂) at about 45°C.

- Fluoride forms soluble complexes with Al³⁺ thus maintaining a high dissolution rate.
- Produces a rougher surface for less metal removal than with caustic etching.
- Less sensitive to alloy variations and can be better at removing die lines, hot spots and streaking.
- Less metal dissolution means less waste - a precipitate that contains (NH₄)₃AlF₆.
- Usually followed by a brief caustic etch to produce the appearance wanted by the customer.
- OH&S issues with acidic fluoride solutions
Acid etching versus alkaline etching

Comparison showing that acid etching gives lower (and more consistent) gloss at low levels of metal removal for different AA 6063 alloy variants. There is further gloss reduction after anodising.

Extent of streaking after etching

10 min NaOH

180 s acid etch

60 s acid etch + 20 s NaOH

180 s acid etch + 40 s NaOH

Checkerboard

Different finishes can produce interesting contrasts – not like checkerboard panels

http://www.jamesandtaylor.co.uk/
Designs and signs

Combining masks or photo-resists with chemical milling and anodizing can produce a range of decorative effects.
Mechanically-textured surfaces

Both extrusion and rolling processes can produce textured surfaces which can have their own unique aesthetic appeal, hide surface blemishes or mimic other materials.

Pattern rolling - brushed stainless steel look-alike

Decorative extrusions

www.aluminiumdesign.net
Digital printing

Print onto unsealed anodized aluminium

Printing capabilities
➢ Maximum print area: 2000 x 3000 mm
➢ Resolution: 2880 x 2880 dpi

Seal after printing
Examples of interference colours

Examples of Henkel Spectrocolor 2000

Munk Alu Spectral colours

Examples of Anolok 2 colours
Aurora® was commercialized in Japan in the 1990s using a variant of Anolok 2.

- clear, pastel colours such as blue, green, yellow, orange and pink
- no longer in production.
Optical model

A model predicts interference colours based on the morphology of the anodic oxidation coating and the optical properties of tin and the coating material.

It has been verified by using electron microscopy.

The model shows that colour is very sensitive to morphological differences, which might explain the low rate of exploitation of the technology.

I De Graeve et al, ASST 2009, Leiden
Wasted energy during anodizing

Poor throwing power can lead to a variation of 4 to 8µm over load with 20µm coating thickness.

The current concentrates at edges and corners. And it is lower within box sections. Higher current density leads to thicker anodic coating.

Throwing power is also affected by solution chemistry.
Reduce excess thickness

See chart below

- Low current density is most important in controlling thickness spread
- High acid temperature is beneficial (compare brown and blue)
- Questionable whether acid concentration is significant (compare green and blue)

A lower current density saves energy because less energy is wasted on excess thickness

![Chart showing percentage spread on 22µm thick coatings with different anodizing current densities.

- 165 g/l, 25°C acid
- 220 g/l, 20°C acid
- 165 g/l, 20°C acid

Chart indicates that:

- Low current density results in lower percentage spread.
- Higher acid temperature also reduces percentage spread.
- Acid concentration seems less significant in controlling spread.
**Reduce excess power consumption**

A lower current density saves power because of the lower anodizing voltage. However, higher acid temperature or concentration can degrade the quality of the anodic coating by producing a “soft film”.

Temperatures above 20°C or concentrations above 200g/l are not recommended for applications where soft films are to be avoided.
Surface abrasion tests and “soft films”

“Soft films” are believed to be more susceptible to degradation by weathering. If the outer few micrometres are too soft, unacceptable changes can occur within months of weathering.

Referee test - abrasive wheel (ISO 8251) - wear index < 1.4

Production control test
- manual test with abrasive paper
(Mohs’s principle)

Anodic oxidation coating must not be scratched by glass
## Anodizing and weathering

AA 6063 flat bar extrusion anodized in 165 g/l sulfuric acid to produce coatings 25 µm thick and sealed in de-ionized water at 98 °C for 50 min.

Weathering for 6 months at Banbury, UK (rural).

<table>
<thead>
<tr>
<th>Anodizing conditions</th>
<th>Abrasive wheel test (4.9 N)</th>
<th>Weathering performance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current A/dm²</strong></td>
<td><strong>Temperature °C</strong></td>
<td><strong>Time min</strong></td>
</tr>
<tr>
<td>1.5</td>
<td>16</td>
<td>50</td>
</tr>
<tr>
<td>1.5</td>
<td>20</td>
<td>50</td>
</tr>
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<tr>
<td>1.5</td>
<td>25</td>
<td>55</td>
</tr>
<tr>
<td>1.2</td>
<td>25</td>
<td>70</td>
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</table>
How to reduce anodizing energy consumption

- Low current densities
- High anodizing bath temperatures
- Effective means of dissipating heat from aluminium surfaces to prevent soft films

- Oxalic acid additions to anodizing bath reduces coating dissolution but acid regeneration processes might be difficult
- Pulse anodizing allows heat dissipation during “off” periods but extends anodizing time
- Flow eductors to agitate the anodizing bath but pumping costs are high
Oxalic acid

Oxalic acid can reduce the dissolution of anodic oxidation coatings in sulfuric acid enabling good quality coatings to be produced in slightly warmer baths.

Many proprietary additives are probably oxalic acid or similar organic acids.

Thickness reduction caused by an abrasive wear test applied to 20 µm coatings produced in 170 g/l H₂SO₄ at 20°C with additions of 0 to 15g/l oxalic acid

Heat dissipation using flow eductors

Heat dissipation in the acid can be improved by using flow eductors instead of air agitation

➢ venturi effect to jet acid within anodizing bath
➢ better agitation
➢ higher conductivity because there are no air bubbles
➢ reduced mist emissions

Flow eductor

Recirculated solution

Reduction in orifice size allows entrainment of surrounding solution
Sealing

What is sealing?

“Treatment of anodic oxidation coatings on aluminium, applied after anodizing to reduce the porosity and absorption capacity of the coating, including but not limited to hydrothermal sealing and cold sealing.” Thus, this includes:

- Hot water
- Steam
- Cold sealing
- Medium temperature
- And many other potential methods

The problem with sealing

- Hot water (≥ 96 °C) and steam have high energy consumption
- Formulations based on nickel salts might be controlled because of OH&S and environmental issues
- Anodized aluminium has poor alkali resistance if conventional sealing methods are used
General Motors requirements

GMW 14665 – 3rd edition, 1st November 2016

This specification covers basic requirements for anodic coatings on aluminum and aluminum alloys.

An issue is resistance to car wash fluids.

Exterior Applications.

➢ Class A – Extreme alkaline resistance to pH 13.5. For Class A, a supplemental coating is mandatory. Exterior coloured anodized parts are required to be Class A

➢ Class B – High alkaline resistance to pH 13.0.

➢ Class C – Alkaline resistance to pH 12.0. This performance level may be usable in emerging markets or other areas where environments are known to be mild.
Examples of approaches to alkali resistance

Sol-gel method

➢ Silica coating needs high temperature curing

Siloxane glass (Japanese)

➢ Alkoxy siloxane coating dried at room temperature

Silicate treatment applied to unsealed anodized aluminium

➢ Two-stage with drying after each at 160 °C for 10 min
  1. Sodium silicate solution at 60 °C for 5 min
  2. Fluorozirconic acid solution at 25 °C for 5 min

Silicate treatment applied to sealed anodized aluminium

➢ Sodium silicate solution at 60 °C for 2 min, and dried at room temperature

➢ The prospect of nickel-free cold sealing

➢ Sealing methods that provide good alkali resistance might be suitable for outdoor architectural applications.

➢ But how do we test product quality?
Tests for sealing quality

Referee test

Mass loss (ISO 3210) - immersion in hot chromic / phosphoric acids
- Tests the chemical resistance to particular acids that do not mimic any service environment
- Developed ca. 1970 for hot water sealing only

Production control tests

Admittance measurements (ISO 2931)
- Measures a property related to the porosity of the whole thickness of the coating

Dye absorption (ISO 2143)
- Assesses the absorption capacity of the coating surface

Electrical analogue of anodic coating used in the development of the admittance test: pores $R_1$; cell walls $C_0$, $R_0$; barrier layer $C_2$, $R_2$

## Test requirements

<table>
<thead>
<tr>
<th>CrO$_3$/H$_3$PO$_4$ mass loss test*</th>
<th>Sealing methods</th>
<th>Nitric acid predip</th>
<th>Maximum mass loss (mg/dm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAMA 611</td>
<td>All</td>
<td>no</td>
<td>40</td>
</tr>
<tr>
<td>ISO 7599</td>
<td>Only hot and cold sealing</td>
<td>yes and no</td>
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</tr>
<tr>
<td>BS 3987</td>
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<td>yes</td>
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</tr>
<tr>
<td>DIN 17611</td>
<td>All</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qualanod</td>
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</tbody>
</table>

The application of the mass loss test is inconsistent.

Can we be confident in its applicability to new sealing methods in the future?

* Qualanod and ISO are introducing a chrome-free mass loss test using H$_3$PO$_4$ alone.
Summary

Trends for the future

➢ Reduced use of alkaline etching
➢ More novel design technologies rather than new colouring methods
➢ Technology to reduce anodizing electrical-energy consumption
➢ Silicate-based cold sealing processes
➢ Re-evaluation of product quality control tests