

The Effect of Sealing on Hard Anodized Aluminum

Dr. Xavier Albert Ventura, Laboratory of Electrochemical Research &
Development, Integral Centre, Barcelona, Spain

The Effect of the sealing method on the abrasion resistance of anodized and hard anodized aluminum was studied. Results are presented for a variety of sealing techniques, including nickel fluoride, nickel acetate, nickel sulfate, molybdenum sulfate, cobalt sulfate and cobalt and molybdenum fluorides. Organic surface treatments and polymer and fluoropolymer synthetic treatments are also discussed.

For more information, contact:

Dr. Xavier Albert Ventura
Carabela La Niña, 22-24 bis
08017 Barcelona, Spain
Phone: (34) 932 05 49 36 / Mobile (34) 639 72 10 65
Fax: (34) 933 38 92 31
e-mail: javieralbort@menta.net

Sealing Methods

We review methods for hot sealing or impregnation cold sealing. In this particular case, it will be the cold sealing method.

Cold sealing or impregnation of anodized aluminium is a technique relatively new. Samples of anodized aluminium sealed by this process have been examined using EPMA, TEM, ESCA and SEM techniques. The results obtained have been analyzed and a theory for the mechanism of the cold sealing process is proposed.

The claims for energy saving and other benefits such as appearance of the finished product and the reduction of condensation in the workshop afforded by cold sealing or low temperature impregnation of anodic films has resulted in considerable interest in these systems.

The process originated in Italy in the early 1980's and the properties of the finishes produced using various systems have been reported in the literature. Little work has been published on the subject of the mechanism of these cold impregnation processes, the available references tend to deal with specific features of the systems and are not in complete agreement with each other.

This paper describes work carried out in an attempt to obtain a better understanding of the mechanism of the impregnation process. It is hoped that the results obtained will help to predict the effects of continual use of the system under production conditions as well as giving some indication as to the likely long term performance of these finishes.

The parameters requiring further explanation were considered to be:

- a. What is the structure of the impregnated film?
- b. With what are the pores plugged and to what depth?
- c. How does the chemical composition of the impregnated film differ from that of the conventional hydrothermally sealed finish?
- d. What chemical reactions occur during the impregnation?
- e. Why is the ageing of the films more significant with cold impregnated finishes than with conventionally sealed finishes?
- f. Why do impregnated finishes have an inferior acid resistance to hydrothermally sealed finishes?
- g. Are the present quality control tests used for assessing hydrothermally sealed anodic films meaningful when used to assess cold impregnated finishes?

We are going to analyze a method for anodizing aluminium, using a cold sealing process.

Experimental process

A proprietary cold impregnation process known to perform as well as any of the products on the market, when subjected to the established seal quality tests, was selected for the experimental work described in this paper.

Sample panels, in 6063 alloy extruded flat bar (150 mm x 75 mm x 3 mm) were etched and anodized in the conventional manner. The etch used was:

- sodium hydroxide 60 g/L
- sodium nitrate 30 g/L
- temperature 60°C
- time 10 min

Sulphuric acid anodizing conditions were:

- sulphuric acid 190 h/L
- temperature 20°C
- current density 1.5 A/dm²
- time 50 min

The anodic films were rinsed in the conventional way between each stage of the process before finally sealing in a proprietary ‘cold impregnation’ solution, which had the following nominal composition:

- nickel as Ni⁺⁺ 2.5 g/L
- fluoride as F⁻ 1.5 g/L
- pH as made up 5.6

Where necessary, conventional hot water sealing or unsealed films were used as controls in the experiments carried out.

The conditions for hot water sealing were:

- deionised water containing anti smut additive
- temperature 100°C
- pH 6.0 ± 0.2
- time 50 min

The conditions for cold impregnation were:

- temperature 30 ± 1°C
- time 12 min

In excess of 60 tests panels were processed through 4 litres of the cold impregnation solution during which time any changes in solution composition or pH were monitored.

The quality of the films produced was assessed using standard seal quality tests.

The beneficial effect of ageing cold impregnated anodic finishes upon the response of these finishes to the standard seal quality tests has been reported elsewhere. In this present work the ageing phenomenon was further investigated by storing selected samples of cold impregnated finishes along with hot water sealed and unsealed finishes and recording the weight gain of the samples with respect to time. The ageing tests were carried out at a temperature of 30°C and a relative humidity of 77% to 85%.

The cold impregnated finishes were examined using the Electron Probe Micro Analyser (EMPA), the Transmission Electron Microscope (TEM), the Electron Spectrometer for Chemical Analysis (ESCA) and the Scanning Electron Microscope (SEM).

The EPMA was used to study the distribution of Ni, S and F in suitably prepared cross sections of the cold impregnated films. The TEM was used to look at the morphology of a microtomed cross section of a cold impregnated film. A 10-micron thick film was selected for this examination because it is a more suitable thickness for the microtoming technique. This particular film was impregnated using a freshly prepared solution.

The ESCA technique was employed to examine the original film surface and the surface after the removal of 2, 6 and 13 microns of the anodic films by a mechanical abrasion instrument (Sugar Abrasion Tester, 320 grit 500 g load). The surface being examined was cleaned by Argon ion beam etching for 1 min prior to analysis. This removes any surface contamination caused by the mechanical abrasion of the film.

The film thickness of the samples used for this test was 25 microns and they were impregnated in a fresh solution using optimum conditions (pH 6.0, 30°C).

The concentration of Ni, F, C, O, S, and Al was measured at each level in the film examined.

The SEM was used to examine the surface and a cross section of a cold impregnated film. The back-scattered mode was used for the SEM examination of the cross section to show, by atomic number contrast, the nickel metal distribution in the anodic film.

Based in the explained previous method the experimental process and the analytical done - ESCA, TEM or EPMA- will determine the different sealing tests

1) Weight gain measured test

The samples were initially weighed after two hours from the time of withdrawal from the cold sealing bath, subsequent weight gain measurements were made at various times intervals after this. Weight measurements were made to the nearest ten-thousandth of a gram.

2) Seal quality test

In most applications, the quality of sealing is another critical property of anodized coatings. To a large extent sealing tests have tended to be indirect tests of serviceability of the product. In particular they have been designed for the testing of hydrothermal sealed anodized finishes. For assessing the seal quality of anodized aluminium (where appropriate) the following tests according to the appropriate British Standards and ISO standards were carried out.

a. Phosphoric acid/chromic acid dissolution test (ISO 3210)

Except for taking proper caution because of the toxic nature of the test solution, the test is straightforward and was found to remove the oxide film uniformly. This test is reproducible and can be controlled very accurately. A weight loss of not more than 30mg/dm² is accepted as the maximum for adequate seal quality.

b. Acetic acid/sodium acetate dissolution test (ISO 2932)

This test was also found to be straightforward to use but precautions had to be taken because of the fumes from boiling solution. A weight loss not exceeding 20 mg/dm² is considered satisfactory.

c. Acidified sodium sulphite dissolution test (ISO 2932)

This is an accelerated test used as an alternative to the sulphur dioxide humidity test, but it is very difficult to control because of the operating temperature of 90°C to 92°C, since at the temperature of over 92°C sulphur dioxide is lost rapidly. Experience with these tests has shown that, if the cold sealed samples have passed by the acetic acid/sodium acetate dissolution test they will satisfactorily pass this test too.

This test is mentioned in many specifications including BS 3987 and the Qualanod specification, and all agree that the maximum weight loss in the test for satisfactory seal quality is 20 mg/dm².

Both acetic acid/sodium acetate and acidified solution test are always used after a nitric acid pre-dip. A weight loss of not more than 10 mg/dm² due to nitric acid is an indication of acceptable film quality.

d. Dye spot (absorption) tests (ISO 2143)

In this test, an acid activates the surface of a sealed anodized finish and then a spot of dyestuff is applied, the absorbed colour intensity of applied dye is noted and compared with a standard colour chart. Most specifications accept a residue stain level of 0, 1 or 2 as indicating acceptable seal quality.

e. Admittance test (ISO 2931)

For assessing the seal quality by admittance test, a Fischer Instrument Anotest W8 was used.

Qualanod specification requires a value of not more than 20 µS for a 20 µm coating.

Although these tests are designed for conventional hydrothermal sealing, they have been used for testing the seal quality of cold seal finishes since no specific tests have yet been evolved.

Other applications of chemical conversion for anodizing are the trivalent chrome solutions used in the aeronautical and shipbuilding industry.

Chromate conversion coatings have found widespread commercial and military applications on aluminium alloys and zinc or cadmium electrodeposits. Of particular interest to the Navy are the use of chromate coatings on aircraft aluminium alloys, because of excellent corrosion resistance and the ability to serve as an effective base for paint. The baths used to develop this coating contain chromates (hexavalent chromium), and it is the residual chromates in the coating that are largely responsible for the high degree of corrosion inhibition observed. Chromates are highly toxic, however, and their presence in wastewater effluents is severely restricted. It would, therefore, be highly desirable to develop a coating for aluminium alloys utilizing relatively non-toxic chemicals that could serve as an alternative to chromate coating.

Preliminary studies were conducted with molybdenum solutions to produce thin coloured films (presumably molybdenum oxides on immersed 7075-T6 Al alloy, but that possessed only slight salt spray resistance. With additives, corrosion resistance of about 24 hr salt spray exposure was achieved as, for example, by 5-min immersion at 25°C in the following bath:

- 6 g/l Na₂MoO₄
- 4 g/l Na₂SiF₆

- 5 g/l Na₃PO₄ · 2H₂O
- 2 g/l Benzotriazole

In another study, 20-min immersion of 7075-T6 All alloy in 20 g/l Na₂CO₃ + 10 g/l Na₂SO₄ solution at 50°C produced films of approximately 200 mg/ft², but with only a modicum of corrosion resistance. By sealing these films in certain aqueous solutions, however the corrosion resistance was improved. For example, as much a 72 hr salt spray resistance was attained by immersion of the rinsed carbonate film for 5 min in 10 g/l KMnO₄ solution at 50°C.

Attention was then directed toward the use of trivalent chromium films, such as have found commercial use on zinc plated surfaces. These films offered little corrosion resistance but imparted an attractive blue-white colour to the zinc. It was considered that if trivalent chromium compounds could be formed on aluminium, it might be possible to oxidize part of the film to hexavalent chromium, perhaps by a post-treatment in dilute peroxide or other oxidizing agent. In this way, it might be possible to attain corrosion-resistance films comparable to the chromate without direct use of toxic hexavalent chromium. It should be noted that trivalent chromium is much less toxic than the hexavalent form, as shown in table 1, compiled by the EPA:

TABLE 1
Water Quality Criteria Summary, Concentrations in µg/L

	CAS #	Priority Pollutant	Carcinogen	Fresh Acute Criteria	Published Criteria		Recalculated Values using IRIS, as of 9/90		
					Water & Organisms	Organisms only	Water & Organism	Organisms only	
Chromium (VI)	7440-47-3	Y	N	16	50	170,000	3,433,000	170	3,400
Chromium (III)	1308-14-1	Y	N	1,700				33,000	670,000

1. Low energy consumption.
2. Low chemical consumption.
3. Minimal drag-out losses of relatively harmless materials and, consequently, low environmental impact.
4. Easy bath maintenance (minimal filtration, Ph adjustment, etc.) and insensitivity to seal tank construction.
5. Seal baths that are insensitive to contamination.
6. Coating hat successfully pass all seal test (acid dissolution, dye, sating resistance, admittance, etc.).
7. Sealed coatings that provide good adhesion to polymeric fillers, where necessary, in windows and door frame constructions, for example.

8. Sealed coatings that provide high resistance to crazing and weathering degradation and are easy to clean and maintain

After explaining the different sealing methods, experimental tests and analytical system for TEM, EMPA, ESCA sealing, as well as tests for sealing, quality, weight gain measuring, admittance, and absorption, the Test Selection Guidelines can be determined:

Test Selection Guidelines

Degradation Factors for Sealed Coatings

- Weather: Moisture, temperature, radiation, air contaminants - SO₂, NO_x, Cl
- Chemicals: Acids, Alkalis, salts
- Particulates: Sand, dust, biological
- Use factors: Coating damage, compressive stress, electroplating effects

Classification: What Do Seal Tests Establish?

- Stain Resistance: Dye stain.
- Chemical resistance: Acid Dissolution test.
- Corrosion resistance: Cars, salt spray.
- Electrical resistance: Impedance, fact.
- Weathering, Natural/accelerated: South Florida

Seal Test Correlation Hierarchy

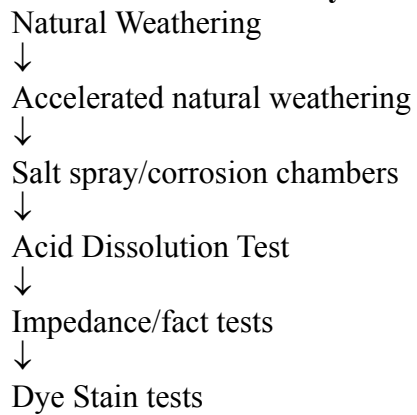


Table 2

**Conversion Coating Line Change-Over
A Drop-In Replacement Using A Natural Coating Systems Chromate-Free Process**

Stage	1	2	3	4	5	6	7	8
Current	Cleaner, Deoxidize	Rinse	Clean/ Etch	Desmut	Rinse	Chorme Phosphate	Rinse	DI
Heat	Yes	Ambient	Yes	Ambient	Ambient	Ambient	Ambient	Yes
Flow	--	Drain	--	--	Drain	--	Filter loop	DI loop
Stage	1	2	3	4	5	6	7	8
NCS Cr-Free Process	NCS Cleaner	Rinse	NCS Activator/ Conditioner	Rinse	Optional Conditioner or Rinse	Seal	Rinse	DI
Heat	Yes	Ambient	Yes	Ambient	Optional Process Dependant	Ambient	Ambient	Yes
Flow [or dump]	[Sewer] ^Δ	Drain	[Sewer] ^Δ	Drain - > <u>2</u>	[Sewer] ^Δ	[Sewer] ^Δ	Filter loop -> <u>4</u>	DI loop -> <u>7</u>

^Δ Depending upon local regulations these baths may be deutralized and discharged periodically if needed.

Table 3
6061 Al Extrusions After 1000 Hours B-117 Salt Spray
Protection Verus Processing Stages

PROCESSING STAGE			% Pitting After 1000 Hours B-117
Activator	Conditioner	Zircon Seal*	
-	-	x	30
-	x	x	3
x	-	x	5
x	x	x	0

* Fluoride-free NCS zurconate composition

Table-4
Properties of Hard-Anodic Oxide Coatings

Electrolyte	Film Thickness (μm)	Microhardness (VNN)		Solar Absorptance		Infrared Emittance	
		1	2	1	2	1	2
H_2SO_4	45-50	440 (425)	416 (385)	0.82 (0.82)	30.83 (0.83)	0.85 (0.84)	0.85 (0.83)
	80-85	430 (400)	- -	0.89 (0.88)	- -	0.88 (0.88)	- -
* H_2SO_4 - (COOH) ₂ + H_2O	47-52	448 (428)	19 386	0.83 (0.82)	0.84 (0.82)	0.86 (0.85)	0.86 (0.84)
	80-85	438 (368)	- -	0.90 (0.89)	- -	0.88 (0.87)	- -
H_2SO_4 - HCl	80-85	406 (368)	400 (362)	0.92 (0.91)	0.91 (0.91)	0.89 (0.88)	0.88 (0.88)
H_2SO_4 - HNO_3	80-85	410 (370)	402 (362)	0.91 (0.90)	0.92 (0.90)	0.89 (0.88)	0.89 (0.87)
H_2SO_4 - (NH_4) ₂ NO_3	80-85	348 (312)	358 (308)	0.91 (0.90)	0.92 (0.90)	0.88 (0.87)	0.89 (0.88)

1 for alloy-1 and 2 for alloy-2

Values given in parenthesis are obtained after sealing of anodic film

Hard Anodizing and Integral Colour Anodizing

Hard anodizing is practically popular for engineering purposes. A thicker film means a hard film since by normal anodizing in sulphuric acid above 20°C or so, the formation and dissolution of the film are balance and usually 25 to 30 micron thickness is maximum, without cooling below 20°C at higher temperature, for example, above 35°C, the oxide film finally disappears during electrolysis. As the film thickens, the colour changes from weak yellow through bronze to black. It appears there exists a colouring voltage when 4DC is used, while in the case of modulated current, even the anode voltage (cathodic polarization being negligible, the peak or surge voltage may happen to be 30 V). Thus coloured and hard films are available. However, in the case of sulphuric acid without any additions the temperature must usually kept below 10°C. EEC has a ample experience of colouring in oxalic acid by the use of AC or AC + DC.

In the author's opinion, the so-called integral colour anodizing such as Kalcolor, Duranodic 300, etc, uses sulphonated aromatic acid or sulphonated higher aliphatic acid with a small amount of sulphuric acid. Aromatic or higher aliphatic group is of itself hydrophobic and together with their big size, they cannot enter into the anodize oxide. Only sulphonation makes them soluble in sulphuric acid solution. During electrolysis, the anodic films and the electrolyte are in a dynamic balanced state and the acid concentrations in the solution and in the films are nearly similar. Sulphuric acid film contains nearly 14 % sulphate and the integral colour films too. Organic group only play a role of attaining the colouring voltage. The existence of excess Al in the film is playing a role of colouring when oxalic acid is gradually added to Duranodic 300 electrolyte, the brownish colour disappears and yellowish oxalic acid colour appears. It is also clear by our experiments the cause of colouring quite different between hard anodizing in sulphuric acid, integral colouring, and the oxalic acid films. The former two show no electroluminescence while the latter shows EL during anodizing and also shows photoluminescence (PL) by UV irradiation on the film. As it may be clear now that chromic acid film contains ca. 3% Cr₂O₃, oxalic acid film ca. 3 % oxalate and sulphuric acid ca. 14 % sulphate and has sulphuric acid coating, integral colour coating contain Al and some sulphate. Therefore, integral colour coating electrolyte operation at 25-28°C, without strong cooling, may replace sulphuric acid hard coating below 10°C. The colour of oxalic acid film comes from another origin. Carboxylate ions which entered in the film is in an excited state and at about 40 V, they convert into tarry products resulting in yellowish or reddish brown colour. This film also belongs to 'semi-barrier' and may have 'colouring' voltage but the mechanism is totally different.

Improved Organic Acid Hard Coating With High Breakdown Voltage (High Dielectric Strength)

A new organic acid process for integral colour was developed by Ventura and co-workers, complying with the needs of hard, smooth, lustrous and high electric breakdown voltage from the EEC advanced electronic industry. A unique and creative designing in bath construction, cathode locations, racking and improvement of anode throw and way of cooling and clearing at least 5000 V/100 micron or more and Hv above 450°C. The operation conditions and film properties are quite different.

- Electrolyte:
 - Oxalic acid 80 g/l
 - Formic acid 80 g/l
- Counter cathode:
 - Graphite
- Temperature:
 - 5-40°C C.D. 2-6a/dm², DC

Pre-Treatment

As pre-treatment it is especially preferred, the elimination of acidic and alkaline fumes like NO_x, SO_x, etc., disposal of P and N compounds, waste recovery and recycles or non-utilization of such toxic material, halo gas. By degreasing with NaOH (with or without chellating agent like gluconic acid), the addition of sodium silicate precipitates sodium aluminium ortho-silicate (Zeolyte) and most of Na h and gluconic acid, if any, are recycled. Zeolyte is used in various ways such as absorbent, builders for detergent instead of sodium tri-polyphosphate, the use of which is now phoibited in the EEC ir order to prevent ithe growth of alga, weeds, etc., in rivers, lakes and inland sea. In order also to replace conventional chemical polishing baths, main constituents of which being phosphoric, nitric and sometimes hydrofluoric acids, the author proposed sulphuric acid based bath. Both acids are very similar in properties (chemical attack, viscosity and polish-capacity). Only sulphuric acid on aluminium is severe. If this is difficulty is overcome, the finish is rather clear than by phosphoric acid by which the finish happens to show iridescent (blue-reddish) tone which often strengthened by wiping. Sul.phuric acid is added with magnesium, cobalt sulphated and some clathrate compounds like zeolyte referred to above will suppress the attack and absorbs acid gas and fumes. Of course phosphoric-nitric acid is easier to handle. Sulphuric acid gives very clear and billiant surface. Zeolyte is also usable for suppressing alkaline fume by degreasing operations.

Table 3. Comparison of Sealing Effect

	Corrosion Resistance	Degree of Sealing mg/dm ²	Additional Sealing HotWater 60°10 min.
L-100 NiF ₂ , 5 g/l	50 s#	10.6	60 s
Zr-001 2 g/l	60 s	8.4	120 s

10 micron film, 10 min. sealing, ageing 1 day (36°C), no final sealing

Corundum and Rubi Films

Anodized Al in the low temperature melts of bisulphate such as NaHSO₄, KHSO₄, and NH₄HSO₄. The simple salt or their mixtures melt at 100-1600. Cand anodizing was done with Ti as cathode in these melts at, say 1,0 A/dm² to form white extra hard corundum films which can be made as thick as 100 micron or more. Sparking and luminescence are evidenced during anodizing. Theoxide consists of alpha-Al₂O₃ which has been converted from the initial amorphous through gamma (face-centred cubic) to alpha-Al₂O₃ (close-packed hexagonal). This is a typical example of electro-oxidation and electro-thermic transition reaction at localized area of Al anode surface. Although the film is coarse and porous and cremic-white (d = 2.96) against compact corundum (d = 4.0), it is dramatically resistant to tangential abrasion and chemically very stable, attacked neither by alkali nor acid nor even by HF. The film can be impregnated with oils, inorganic and other functional material. The corundum coating is finding applications in heat-resistant ductile Al wire for magnetic coils (500°C), business machine parts where extreme wear resistance is required, solid type capacitors. Cock et al. Demonstrated a possible pretreatment to improve stress-cracking performance of Al alloys in aero-space applications.

The first conventional sulphuric acid to form porous type films which are then immersed in ammonium sulphate solution, subjected to anodizing in bisulphate melt. The films were converted to alpha type and doped Cr played a role of formin ruby film. The films are rather coarse and pink, but under UV light irradiationm, the film shows a fascinating deep red colour. They applied various salt solutionsm but Cr gave best results. The process may be applied for decoration, illumination, electronics displays,laser applications, etc.

SUMMARY

Key Points in Test Selection

- Using tests from several groups increases field reliability
- Seal technologies have significant effect on test results and ultimately field performance.
- Best reliability is obtained through natural weathering or accelerated environmental exposure.
- The best test program with low acceptance criteria will not assure field performance.

CONCLUSIONS

- I. Both sealed and unsealed films gain in weight with time. The weight gain is much greater for sealed than unsealed films.
- II. According to the phosphoric acid/chromic acid dissolution, dye absorption and admittance tests ageing has not influence on the unsealed film.
- III. A substantial increase in weight gain with ageing for nickel fluoride cold sealed finishes is due to the nickel ion which has a catalytic effect on the hydration process, hence influencing the results of the seal quality assessment.
- IV. The cold sealed finish passed the following tests after:
 - ISO 3210 Phosphoric acid/chromic acid, 7 hours
 - ISO 2932 Nitric acid, 7 hours
 - ISO 2932 Acetic acid/sodium acetate, 24 hours
 - ISO 2932 Acidified sodium sulphite, 7 hours
 - ISO 2143 Dye absorption, 4 hours
 - ISO 2931 Admittance, 14-30 days
- V. The hydration reaction on samples treated in nickel fluoride cold seal solution is continuous. The rate at which the hydration takes place depends on the temperature and humidity.
- VI. Seal quality standards are tools to achieve durability and reliability for anodized coatings in field service.
- VII. On-going revisions by the standards organizations produce improves standards and product performance.
- VIII. No single quality assurance procedure exists to accurately correlate with various environments.

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