“Sealing Method fr Anodizing Aluminium and Hard Anodizing and Test For Seal Quality Of Aluminium

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

Sealing is an important step in aluminium anodizing process. It is used for sealing aluminium extruded profiles, mechanize parts, cosmetic’s plastic holders, lamps, etc. as well as for hard anodizing.

Therefore, it is very important to choose the appropriated electrolyte for capillary pore formation and also porous, non-porous and barrier layers formation. The electrolyte use in this work is sulphuric acid.

Also, it will be reviewed the different sealing with nickel, cobalt, molybdenum salts and we will analyse colour, weight loss and abrasion resistance tests.

Sealing techniques with silicates and fluoropolymers for hard anodizing will be explained.

Dichromate and chromate sealing are not contemplated because they will be definitively proscribed in the European Union at the beginning of 2007. Therefore, we have to search for new sealing techniques with will not produce harmful impact on environment.

For more information, contact:
Dr. Xavier Albert Ventura
Carabela La Niña, 22, 2º, 1ª
08017 Barcelona, Spain
Phone: (34) 933 37 03 22 / Mobile (34) 639 72 10 65
Fax: (34) 933 38 92 31
e-mail:javieralbort@menta.net

The Behaviour of the Porous-Layer Barrier in Aluminium

Anodic Oxidization

Unlike the electrocoating process in which the layer increases towards the electrode outer part, in anodic oxidization the layer growth is towards the inner part of the metal and therefore consuming it.

If we concentrate on the faradic conversion of Al to oxide, we observe that for each gram of metal consumed, l.889 grs of oxide is obtained.

The coating relation is defined as the oxide amount formed per gram of reacted aluminium, which experimental value -double weighting measurement- show us the efficiency of the anodic process.

The classification of the anodized layer during the formation process can be made in accordance with the dissolvent amount of the electrolyte in that layer.

Non-Porous Layer

The non-porous layers are those, which do not retain dissolvent in the formed oxide layer and therefore, are compact, dielectric and thinner. The layer thickness initially depends on the applied potential and temperature. In a dielectric environment if the potential applied is high enough, a strong discharge is produced, thus perforating the layer. We call this effect layers breakage.

The electrolytes causing this type of breakage are aqueous dissolutions of borates, tartrates, succionates, citrates, phosphates and carbonates. The breakage potential for the non-porous layers, oscillates between 500 and 700 V and refers to thickness between 7,000 to l0,000 A. If the applied potentials are lower, the current density becomes almost zero and the layer growth is gradually slowed down until becoming non-existent.

The velocity formation in the initial layer increases lineally in relation to the current density and the coating relation value near to the theoretical value of 1.889 as for a process that has not secondary reactions.

Porous Layers

Porous layers are those, which do not hold dissolvent in the formed oxide layer. They are gelatinous and therefore thick and soft. In the porous layer the coating relation has a value of l.35 to l.46 due to the existing competitive effect of dissolution against that of oxide formation. The porous layer because of its physical characteristics cannot serve the purpose of being a protective layer. The insolubility of the porous layer is achieved through sealing. This seems to transform the superficial layer in small crystalline nuclei of hydrated oxide, which several authors believe to be bohemite.

Principles of Anodizing

The manner in which anodic oxidation differs essentially from the industrial electrolytic processes will be apparent from the following three examples all using sulphuric acid, say 10% by volume, as the electrolyte.

In Figure A, if the electrodes are made of platinum or any other metal that does not dissolve at the anode or positive electrode, oxygen gas is liberated at the anode and hydrogen gas at the cathode. No metal is dissolved in the acid.

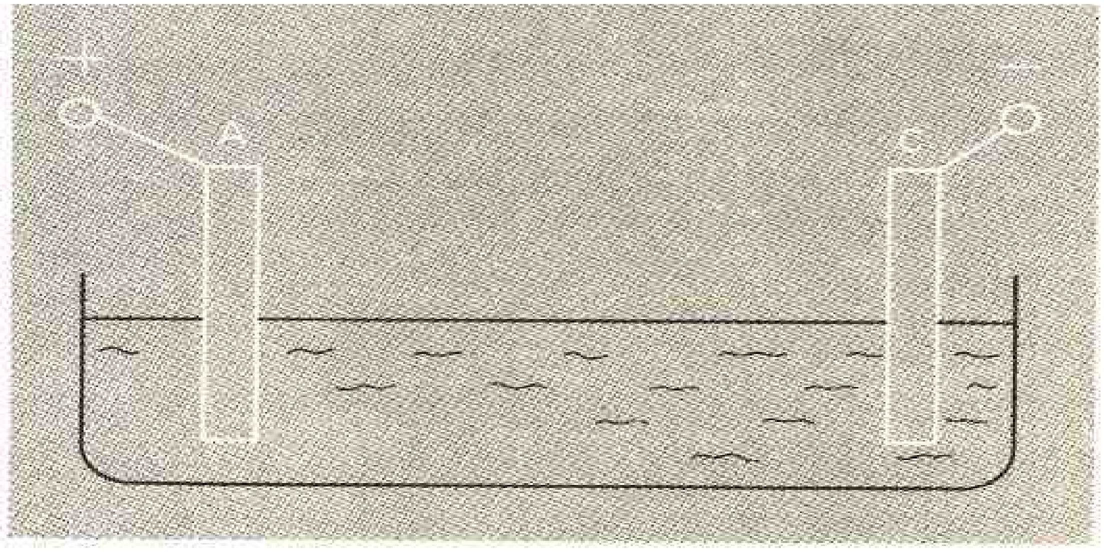

Figure A, Current Entering and Leaving Solution in Anodizing

If the anode is made of copper it will dissolve in the acid and will be re-deposited on the cathode. This is the basis of many metal electrodeposition processes. In commercial production with soluble metal anodes little or no gas is evolved at the anode and cathode.

When the anode is aluminium, the cathode, in commercial practice, is either aluminium or lead. When current is passed the aluminium anode does not dissolve away like copper, nor is oxygen evolved in quantity. Instead, most of the oxygen that would have been liberated combines with the aluminium to form a layer of porous aluminium oxide. Hydrogen is liberated at the cathode.

The amount of aluminium oxide formed is directly proportional to the current density and time, *i.e.* to the quantity of electric current used. The progress of the formation of the anodic coating depends upon the chemical composition of anodising electrolyte and the chosen conditions of electrolysis. Some anodising electrolytes have little or no solvent action on the oxide coating so that the process soon ceases, leaving a thin film usually referred to as a barrier-layer-type coating, the thickness of which is solely governed by the applied voltage and approximates to 1/700 μm per volt. This type of coating is typically produced in solution of borates, boric acid or tartrates.

If the electrolyte has some solvent action, then a porous film is formed and the oxidation process can continue leading to the production of relatively thick films, as for example in sulphuric acid. Eventually the rate of film formation is balanced by the rate of solvent attack, but this stage of the process is avoided in commercial practice.

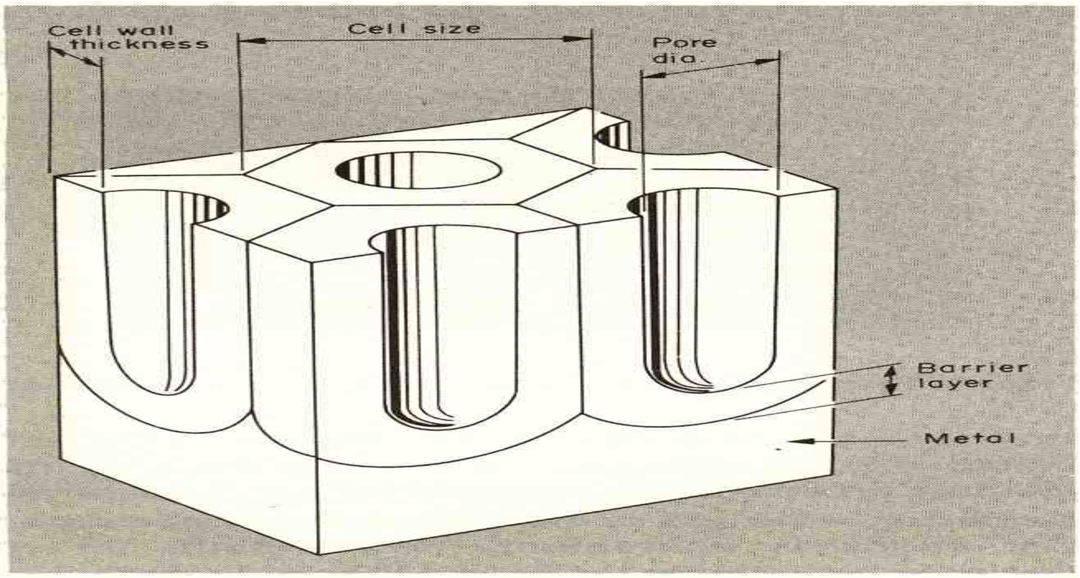

Figure B. Microstructure of Anodic Film

Table 1 - Film Density Values

Al_2O_3 fused ceramic	3.8 – 4.0 g/cm^{-3}
α- Al_2O_3 corundum	3.97
γ- Al_2O_3	3.5
$Al_2O_3.H_2O$ boehmite	3.014
$Al_2O_3.H_2O$ bayerite	2.42 – 2.53
Thin barrier layer	2.9 – 3.2
Minimum ion anodic films*	2.32
Unsealed anodic film*	2.40
Sealed anodic film*	2.60
Films on Al-Cu alloys: films produced at 40-50°C	1.8 – 2.1

Table 2 - Anodic Reactions Of Anodizing

Film Formation	$2Al + 60H^{-} \rightarrow Al_2\ OH_3 + 3H_2O + 3\varepsilon$
Film Dissolution	$Al \rightarrow Al^{3} + 3\varepsilon$
Oxygen evolution	$4OH^{-} \rightarrow H_2O + O_2 + 4\varepsilon$
Sulphate oxidation	$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\varepsilon$

Film Porosity

The pores have advantages and disadvantages: the former offers opportunity for incorporation of new phases especially dyestuffs to modify properties. The latter includes an essential need of pore sealing to produce a stable anodic film. The extent of porosity affects these properties and to yield hard films it should be low by low by selection of appropriate parameter levels (see Table 3)

Table 3 - Choice Of Process Variables
For Optimum Hard Anodizing (After Kape)

Parameter	Favoured conditions for hard anodizing
Temperature	LOW
Electrolyte concentration	LOW
Anodizing time	HIGH
Correct choice of alloy	Cu and Si FREE
Current density	HIGH
Agitation of electrolyte	HIGH
Type of current	PULSED or AC + DC

The exact meaning of hard can be seen from typical values (see Table 4) that show that aluminium itself is soft, the hydrated or porous film moderately hard and the pure oxide very hard. In the case of barrier layer films an acid is chosen in which the dissolution reaction does not occur and pure passivity takes place without diffusion or mass transport controlled film growth.

Table 4 - Hard Anodic Films: Hardness Values

Pure aluminium	50-55 VPN
Aluminium alloys	60-140
Boehmite, $Al_2O_3.H_2O$	250-600
Pure alumina, Al_2O_3: sapphire corundum	1200 1800

The link between film hardness and porosity is well-established, for example Wenick, Pinner and Seasby have long quoted data for anodizing at 4A/dm^2 for 30 min. to yield films having the following properties:

- 1°C porosity of 10-14% - Hardness of ~500VPN
- 30°C porosity of 24-26% - Hardness of ~300VPN

Porosity occurs as the result of two dynamic competitive processes: film formation and film dissolution. The factors affecting porosity can be simply listed:

Acid concentration	-porosity increases with concentration
Current density	- porosity decreases with CD
Temperature	-porosity increases with temperature
Thickness/time	-porosity increases with thickness

Note that there are critical compositions for each acid:

Boric acid	- no pore formation
Sulphuric acid	- 7-22% acid yields porous film
Hydrochloric acid	- no film formation

The evidence for porosity can be summarised in relation to the processing characteristics and the consequences for the product film.

Porosity and Density

The porosity has a marked practical effect and that is that it changes the density of the film. This has implications for standard thickness measurements and has been discussed elsewhere. The experimental option for measuring thickness include

Taper micro-section	- absolute method
Strip and weight	- value of d required
Eddy current meter	- requires calibration
Optical methods	- requires calibration

The fact however can be summarized as follows:

- Density values vary from 2.3 to 3.3. g/cm^3, a variation of 40%
- The uncertainty is recognized in BS6161

- Standard values are quoted as:
  - sealed films 2.5 g/cm^3
  - unsealed films 2.4 g/cm^3

The uncertainties in density values include the determination characteristic that thickness measurement is taken at a point by microscopy, that film weight are averaged over and area, and that small changes in anodizing have local effects on thickness which are difficult to define. For thicker films, the uncertainty need not to be critical but for thin films (eg. <3µm thick) where surface optical properties are critical the error can be a serious quality measuring difficulty.

The importance of porosity is that it has a marked effect on the film's mechanical properties, the ability to take-up dyestuffs, the need for a sealing process step and development of 'epitaxial'.

The structure of the porous type of anodic oxide coating is shown diagrammatically in figure B, and can be seen to comprise hexagonal columns each with a central pore which reaches down to a thin compact barrier layer which is continuously formed and transformed into the porous form during the process.

The diameter of the pores and the thickness of the barrier layer for any given electrolyte and temperature are proportional to the applied voltage. Thus by varying the anodising conditions it is possible to alter the physical properties of the coating, such as the hardness, abrasion resistance and the density.

From the foregoing it will be appreciated that anodising is a conversion process so that the appearance and other properties are completely dependent upon the composition of the aluminium and its surface condition. Anodizing, therefore, differs fundamentally from processes such as electroplating where a layer of metal is applied over the base metal surface.

After anodising the film is usually sealed by a hydration process to minimize the initial porosity. For some special applications physical sealing with an organic material such as oil, is desirable.

Film Hardness

Vicker's Hardness on the cross sections of hard anodised films 20-25°C, 2-6 amp/dm^2 60-110 µm) produced with the two agitation methods is compared in Figs. I and J. In these figures, the biggest rhomboids of diamond indenter trace indicate softer film. In the ordinary air agitation method, the film hardness decreased stepwise from the inner to outer layers of the film (HV 410 → HV 260). The hardness was almost constant in films produced with micro explosive air agitation (HV 430-410). In the ordinary air agitation method, it is assumed that since the films layers produced in the early period of electrolysis are gradually dissolved because of generated Joule Heat and becomes coarse, the film becomes softer as it comes close to the surface. It is believed that in the micro explosive air agitation method, the hardness becomes uniform owing to favourable dispersion of Joule Heat. Elevation of surface hardness contributes to improvement of abrasion resistance.

Table 5 – Change of Anodizing Bath Voltage

Agitation Method	Air volume (L/min/M)	Bath Voltage (V)
Without Agitation	---	14.6
Normal Air Agitation	22	15.1
Micro Explosive Air Agitation (Weak)	22	17.0
Micro Explosive Air Agitation (Middle)	44	17.5
Micro Explosive Air Agitation (Strong)	66	17.5

(Anodizing Condition: 1 A/dm^2, 25°C, Al 6063/6065)

Figure 1 – Rough Sketch of Constructions of Films by Both Agitation Methods

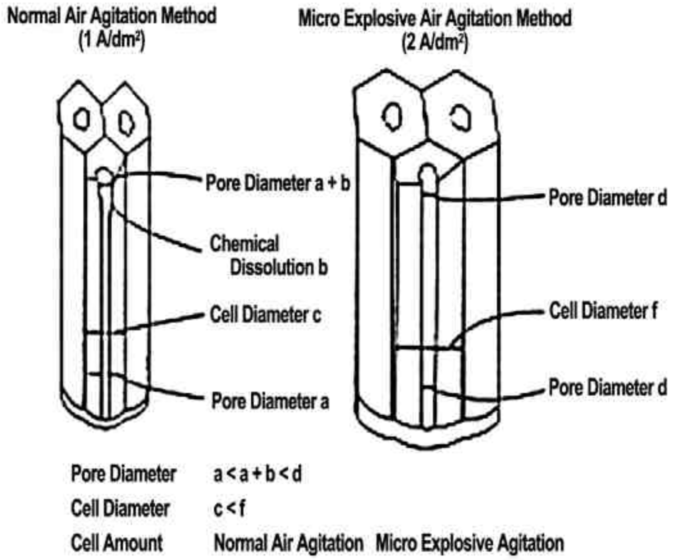

Table 6 – Distribution of Film Thickness at Bath Agitation Method on Aluminium Articles

Agitation Method	Anodizing Temperature (°C)	Film Thickness (μm)	Absolute Reflectivity (%)
	______	_____	88.4 - 95.0
Normal Air Agitation	20	13	72
	20	25	73
	22	13	74
	22	25	73
	26	13	72
	26	25	71
Micro Explosive Air Agitation	19	13	75
	19	25	72
	22	13	75
	22	25	72
	26	13	75
	26	25	72

(Anodizing Condition: 2.0 A/dm^2 : 45 min)

Table 7 – Relation Between Current Density & Standard Deviation of Film Thickness at Both Air Agitation on Aluminium

Agitation Methods	Anodizing Conditions (25°C)	Disposition of Jigging	Average of Thickness at 9 Positions (μm)	Standard Deviation (μm)
Normal Air Agitation Method	1-3 A/dm^2 25 min	Parallel-ward	7.9	0.428
		Vertical-ward	7.7	0.868
	1-3 A/dm^2 15 min	Parallel-ward	8.7	0.757
		Vertical-ward	8.7	1.281
Micro Explosive Air Agitation Method	1-3 A/dm^2 25 min	Parallel-ward	7.9	0.262
		Vertical-ward	7.9	0.403
	1-3 A/dm^2 15 min	Parallel-ward	8.9	0.498
		Vertical-ward	8.9	0.710

(Unit: μm)

Table 8 – Relation Between Current Density & Standard Deviation of Film Thickness at Both Air Agitation on Aluminium

	Normal Air Agitation			Micro Explosive Air Agitation		
	Upper	Middle	Below	Upper	Middle	Below
Specimen 1	16.5	17.8	19.8	17.0	17.7	18.4
Specimen 2	16.4	17.8	19.2	17.1	17.2	17.9
Specimen 3	16.6	17.8	19.0	17.9	18.0	18.4
Specimen 4	16.6	18.0	19.2	17.8	18.2	18.5
Average Thickness	16 - 19.8 μm			17 - 18.5 μm		
Standard Deviation	0.995			0.6825		

Table 9 – Relation between Current Density & Standard Deviation of Film Thickness at Both Air Agitation Methods and Aluminium Article

Anodizing Condition	Normal Air Agitation (μm)	Micro Explosive Air Agitation (μm)
1.0 A/dm^2 (25°C, 45 min)	0.472	0.390
1.5 A/dm^2 (25°C, 30 min)	0.892	0.501
2.0 A/dm^2 (25°C, 25 min)	1.622	0.721

(Thickness: 18 μm)

Basic Mechanisms of Sealing

Sealing Treatment

The hard oxide film formed during anodizing consists mainly of aluminium oxide and approximately 13-17% by weight sulphate ions, incorporated from the electrolyte into the oxide lattice. The distribution of sulphate ions is somewhat dependent on process conditions but diminished from the outer surface of the oxide towards the barrier layer.

Porosity of the coating decreases when higher voltages, and lower electrolyte concentration and temperature are used, as it is the case for hard anodising. It is of direct importance for the corrosion properties and wears resistance of the film. Therefore, corrosion and sealing data obtained from different anodic films cannot be directly related, increasing the possibility for unsatisfactory sealing or extensive softening of the film.

To improve corrosion resistance of anodic films the pores of the oxide have to be closed, minimising specific surface and converting the aluminium oxide to a more stable form. Sealing in boiling distilled water is one of the simplest techniques available for closing the pores, by

converting the aluminium oxide to a hydrate -most probably bohemite- which involves an increase in volume, swelling the pore walls till the pore closes.
The sealing treatment used to seal anodic oxide coatings can be generally divided in to hydration sealing, impregnation sealing, and some miscellaneous treatment like electro deposition of paint.

Sealing By Hydration
The basic reaction in hydration sealing is the conversion of amorphous aluminium oxide to a stable, hydrated form, most likely boehmite.

$$Al_2O_3 + H_2O \rightarrow 2AlOOH_2$$

Aluminium oxide Water → Boehmite

Normally it is done by putting parts in boiling water, with some appropriate bloom preventer. The use of steam to seal de coating is also an option and has some advantages and disadvantages when compared to hot water sealing, but involves the same basic reaction. Because the sealing process is diffusion controlled, the rate of sealing is not linear with time, which means that the rate of conversion diminishes progressively with time. More oxide to the surface of the coating will be converted to bohemite than towards the barrier layer because of the rapid blocking of the narrow pores. From investigations of the sealing process, optimum conditions for hot water sealing should be:

- Demineralised water
- pH = 5.5 – 6.5 buffered
- Temperature > 95°C
- Surface active agent
- Sealing time 2-3 min/µm

Sealing according to this guideline means that the post-treatment is about half of the total process time when one has to seal a 50 µm hard anodic film. This is not common practice for hard anodic films because the wear resistance especially of the upper region of the layer, has decreased due to the formation of the much softer bohemite.

Impregnation sealing
Impregnation sealing of anodic coatings involves the chemical conversion of the aluminium oxide into complex aluminium salts, thereby blocking of the pore between 20 and 32

Impregnation sealing can be done in hot and cold solutions containing additives like nickel salts, dichromates or silicates. The most recent additions to these have been the cold sealing process operating at room temperature or somewhat elevates temperatures.

Cold Sealing

Cold sealing processes operates at temperatures between 20 and 32°C in a solution containing nickel and fluorides. The sealing medium enters the micropores leaving precipitates like $Al(OH)F_2$, $Ni(OH)_2$ and $AL(=H)_3$ in approximately the upper 5 µm of the film.

Some of the possible reaction that occurs are:

$$AL_2O_3 + 6F^- + 3H_2O \rightarrow 2AlF_3 + 6OH^-$$

$$AL_2O_3 + 6F^- + 3H_2O \rightarrow 2Al(OH)_3$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$$

This effectively blocks off the pores, although chemical resistance increases with time due to moisture uptake and therefore further reaction and closing of the pores. Using the process at higher temperature results in poorer seal quality. Normally a post rinse temperature to promote seal quality follows the process. A typical formulation for a cold seal is presented below:

Ni^{2+}	1-2 g/l
F^-	0.5-0.6 g/l
pH=	5.5-6.5
Temperature	20-32°C
Surface-active agent	
Post rinse in water, T>60°C	
Sealing time 0.8-1.2 min/µm	

Post treatment to accelerate hydration of the coating is normally performed in hot water with the optional addition of nickel salts. The nickel in the coating promotes the natural ageing process. In some cases some cobalt is added to mask the green colouration by high nickel concentration in the coating.

Looking at the chemical reactions that occur and reaction products formed, it is generally assumed that wear resistance is decreased during cold seal treatment.

Medium Temperature Sealing

Medium temperature seals mostly employ nickel salts and some surfactants to increase sealing speed. The increase is sealing speed is also assisted by the presence of nickel, which functions as a catalyst for the conversion of aluminium oxide to bohemite.

Advantages of this type of seal are the slight reduction in operating temperature, usualy between 70 and 90°C, and a higher tolerance for silica in the water.

It is also extremely useful to prevent bleeding out of certain dyes by forming a metal salt with the dye. As with hot water sealing, partial transformation of aluminium oxide to boehmite take place, resulting in a decreased wear resistance.

Dichromate Sealing

Dichromate sealing is based on the following reactions between potassium dichromate and bohemite.

$2(OAlOH)$	+	$KHCrO_4$	→	$2(OAlCrOH_4)$
boehmite		potassium chromate/dichromate		aluminiumoxychromate
$2(OAlOH)$	+	$KHCrO_4$	→	$2(OAlCrOH_4)$
boehmite		potassium chromate/dichromate		aluminiumoxydichromate

Which reaction dominates depends on the pH of the solution. The preferential reaction of dichromate with the oxide prevents hydrothermal sealing, leaving the pores partially blocked by the aluminium oxydichromate, but not closing them entirely. Sealing times are normally in the range3 of 20-30 minutes, although sometime longer times are specified.

Sealing in dichromate gives a very good corrosion resistance and improves fatigue strength of anodic coatings. Because hydration of the coating is largely prevented, wear resistance should only be slightly affected.

Silicate Sealing

One of the possible mechanisms for silicate sealing is based on the formation of silic acid in the pores of the aluminium oxide, which in turn reacts with the aluminium hydrate to form the relatively hard aluminium silicate. The optimum ratio for soda-silicate should be around 1:3.3 (Na_2O: SiO_2). A typical procedure for silicate sealing is boiling the parts for approximately 30 minutes in a solution containing 5% sodium silicate. The effect on hardness and wear resistance is reported to be minimal, mainly because no boehmite is formed.

Miscellaneous Sealing Methods

Sealing by electrode position
Fluoropolymer impregnation

Experimental Procedure

Material

6063, 6065 and 1015 blocks (10.0 x 10.0 x 0.5 cm) were used in all experiments

Pre-treatment

The blocks were cleaned in a mild alkaline degreaser for 10 minutes after which they were rinsed in tap water. The blocks were etched in 130-180 g/l caustic soda solution, followed by rinse in tap water for 5 minutes. Deoxidising for 5 minutes took place in a desmutting solution containing a mixture of hydrofluoric, nitric and chromic acid.

A final rinse in demineralised water was given before the blocks were transferred to the anodizing tank.

Hard Anodizing

Anodizing took place in a conventional electrolyte containing 190-225 g/l sulphuric acid and aluminium, between 5-6- g/l aluminium. The temperature of the electrolyte was maintained at -2 to 5°C, the electrolyte was vigorously agitated with air to keep a uniform temperature in the bath and to allow for rapid heat transfer from the coating to the electrolyte.

The blocks were anodised by ramping to 2.5 A/dm^2 in 5 minutes and keeping a constant current density until a layer thickness of 60 ± 2 um was reached. The power then was switched off and the parts were transferred to an intermediate rinse followed by a thorough rinse for 20-25 minutes in demineralised water. Sealing of the blocks directly followed by rinsing.

Sealing

The conditions for sealing are specified in Appendix 1. After sealing, all blocks were shortly rinsed in demineralised water, whipped dry with cloth and left to dry for 30 minutes.

Directly following the coupons were weighed with an analytical balance and prepared for further testing.

Test Methods

To evaluate the effect of different sealing methods on hard anodic coating, the following test methods were used:

- Weight loss test, ASTM B-680
- Salt spray testing, ASTM B-117
- Abrasive wheel testing, ISO 8251
- Vickers hardness test, ISO 4516

Weight loss test

The weight loss test, also called acid dissolution test (ADTV). Is actually a test for chemical resistance and can be drastically influenced by the sealing medium, as is the case for dichromate sealing and other impregnation methods.

After weighting the samples and a short immersion in nitric acid, they are placed in a stirred solution containing 25 g/l chromic acid and 35 ml/l orthophosphoric acid (85%) maintained at a temperature of 40±2°C. After 25 minutes the parts are removed from the solution, washed in demineralised water, dried and weighted to obtain the mass loss per surface area.

Abrasive wheel testing

ISO 8251 specifies a method of test for determination of the wear resistance of anodic oxidation coating by means of an abrasive wheel wear test apparatus. The anodic coating is abraded by a reciprocal motion against a strip of silicon carbide, attached to the outside of the wheel.

After each double stroke (1 reciprocal movement) the wheel turns slightly, thereby bringing an unused portion of the abrasive strip into contact with the test area.

The decrease in coating thickness or mass obtained is a measure of the wear resistance.

Because anodic films are somewhat softer at the outside, wear is divided into post wear and initial wear, the latter case representing approximately the first 1500 cycles.

In this research decrease in mass was taken as a value for wear resistance, because loss of material is not desirable for a lot of applications, especially when wearing low friction or narrow dimensional tolerance are demanded. All samples were stored in desiccators for five days before testing took place.

Hardness testing

Hardness resting of anodic coating according to ISO 4516 is done with a diamond indenter with a low load, after which the size of the indentation is measured and the hardness value can be calculated. Specimens for micro-hardness testing were prepared by embedding cross sections of the coating in thermosetting resin, followed by polishing. The hardness profile across the layer was determined using a 25 p. load.

The determined hardness value by Vickers not always represents the material performance when wear is considered, and caution should be regarded interpreting these data.

Also initial wear of anodic coating is related to the upper few microns of the oxide, which cannot be accurately measured by this method, normally a minimum distance of 5 µm is specified between indentation mark and resin.

Salt spray testing will not discussed in this paper because tests are still running, although I will make some comments about some intermediate results later.

Results and Discussion

Weight loss test

Looking at the data obtained from the weight loss experiments (Appendix 2, Table 10), the high mass loss encountered with the dichromate is, as earlier mentioned, due to the nature of the test. However, still can be seen that weight loss decreases linear with time. The lowest weight loss was obtained by the medium temperature nickel acetate seal and the polymeric sealer who resisted attack totally. Anodic films sealed in hot water reached after 120 minutes acceptable level for weight loss, although according to the data, the rate of sealing already sharply decreased after 25 minutes. It is questionable if corrosion resistance is substantially improved by prolonged seal times in hot water. Cold sealing systems show a surprisingly constant weight loss when a hot water dip is employed, and are hardly influenced by prolonged sealing times. If this test is able to discriminate between different sealing times is unclear, although reproducibility was high and some differences can be seen between the different cold seals. The more recent development medium temperature seal did not show any improvement when compared to the hot water treatment and cold sealing systems.

Table 10 - Comparative Results for Weight Loss ASTM B-680

Post Treatment	Sealing Time	Weight loss (mg/dm^2)
Hot water seal	15 min	78
	30 min	55
	45 min	45
	60 min	45
	120 min	30
Medium temperature seal	10 min	420
	30 min	120
	60 min	15
Dichromate seal	5 min	800
	10 min	700
	15 min	400
	20 mn	200
Medium temperature silicate seal	90 sec	800
Organic sealer	contact	0
Medium temperature seal	60 min	100
High speed nickel acetate	30 min	120

Table 11- Hardness Testing - ISO 4516

Post Treatment	Sealing Time	Micro Substrate	hardness (25 p) side<------------>	HV (n=8) surface oxide
Hot water seal	15 min	430	430	330
	60 min	500	430	425
Medium temperature seal A	60 min	500	500	400
Medium temperature silicate seal	90 sec	450	440	440
Organic sealer	contact	460	460	410
Medium temperature seal B	60 min	460	480	450
High speed nickel acetate	30 min	425	410	450

Sealing in cold seal media increases mass loss in abrasive wheel test, while the post treatment in hot water increases mass loss even further. Cold seal C showed some improvement although weight loss still was increased. Sealing for prolonged times in cold seal solutions decreased weight loss slightly.

Dichromate, medium temperature silicate seal, high-speed nickel acetate and 15 minutes hot water seal affected weight loss only slightly indicating a low level of hydration.

Weight loss for samples sealed in medium temperature seal B and C was high, even when compared to samples that were sealed in hot water for 50 minutes.

Hardness testing

Influence of most sealing systems on micro hardness is limited. However, for cold sealed samples a certain decrease in the outer regions of the oxide is observed.

This can possibly explain why higher mass loss was observed with abrasive wheel testing. However, sealing in hot water and medium temperature with seal A, B and C, showed increased or unaltered micro hardness values with increased mass loss during abrasive wheel test.

Looking at the results of ADT and abrasive wheel test, seal time indicated by suppliers are somewhat high for hard anodised films. Shorter treatments in the range of 15 to 20 minutes with conventional sealing methods are recommended to maintain hardness and abrasion resistance. Minimal times for good corrosion protection will be derived from stain resistance, dye spot and salt spray tests, and will be presented in the following paper.

Appendix 1
Post Treatments

POST-TREATMENT NR	PROCESSES PARAMETERS		SEALING TIME
0 None			
1 Hot water seal Demineralised water with bloom Preventer Systoseal seal	T (°C)	95-100	15/30/45/60 min
	Systoseal seal	0.5 vol %	
	pH=	5.5-6.0	
	Time	2-3 min/micron	
2 Medium temperature seal A Nickel acetate seal with cobalt Addition and bloom preventer	T (°C)	95-100	20/30/60 min
	Nickel acetate	5-0-6.0 g/l	
	Cobalt acetate	0.6-0.7	
	Bloom preventer	0.1 vol %	
	PH=	5.5-6.0	
	Time	2-3 min/micron	
3 Dichromate seal Potassium dichromate seal	T (°C)	96-100	25 min
	Potassium dichromate	40-60 g/l	
	pH=	5.5-6.1	
	Time	Anodizing time	
4 Medium temperature silicate seal Commercial additives. Composition unknown	T (°C)	50	2 min
	[..]	15 V %	
	pH=	11	
	Time	30-90 s	
5 Organic sealer Polymeric impregnation, leaves Non wetting surface	T (°C)	30	45 sec
	[..]	40 V %	
	PH=	9	
	Time	Contact	
	Drying	75°C	

6 Medium temperature seal B
Metallic salts and surfactants,
nickel free and fluoride free

T (°C)	>85	60 min
[..]	5 V %	
pH=	6-6.5	
Time	1 min/micron	

7 Medium temperature seal C
Mix of surfactants.

T (°C)	>90	60 min
[..]	0,5	
pH=	5.5-6.0	
Time	1 min/micron	

8 High speed nickel acetate seal
Mixture of nickel acetate and
organic salts

T (°C)	>90	35 min
[..]	5 V %	
pH=	6.5	
Time	0.5 min/micron	

9 Cold seal A
NiF-based cold seal.
Hot water dip for improved
Corrosion resistance

T (°C)	20-35	20/30/60 min Followed by H.W dip T = 70°C, Time = 0 or 10 min
[..]	4 V %	
pH=	5.5-6.5	
Time	0.8-1.2 min/micron	

10 Cold seal B

NiF-based cold seal.
Hot water dip for improved
Corrosion resistance

T (°C)	20-35	20/30/60 min Followed by H.W dip T = 70°C, Time = 0 or 10 min
[..]	5 V %	
pH=	6.2-7.0	
Time	0.5 –1,0 min/micron	

11 Cold seal C
NiF-based cold seal.
Hot water dip for improved
Corrosion resistance

T (°C)	20-35	25 min Followed by H.W dip T = 70°C, Time = 0 or 10 min
[..]	4 V %	
pH=	5.5-6.5	
Time	0.5 min/micron	

Appendix 2 - Results

Nr.	**Post Treatment**	**Sealing time**	**Weight loss mg/dm2**
0	Non sealed	0 min	580
1	Hot water seal	15 min	75
		30 min	50
		45 min	45
		60 min	40
		120 min	30
2	Medium temperature seal A	20 min	400
		30 min	135
		50 min	15
3	Dichromate seal	5 min	800
		10 min	670
		15 min	390
		25 min	200
4	Medium temperature silicate seal	2 min	820
5	Organic sealer	Contact	0
6	Medium temperature seal B	60 min	110
7	Medium temperature seal B	60 min	80
8	High speed nickel acetate	35 min	120
9	Cold seal A/H.W. dip	5/5 min	100
		10/5 min	90
		5/10 min	90
		10/10 min	80
		30/10 min	60
		60/10 min	90
10	Cold seal B/H.w. dip	5/10 min	60
		10/10 min	65
		30/10 min	50
11	Cold seal C/H.W. dip	25 min	90

Appendix 3

Nr.	Post Treatment	Sealing time	Micro hardness (25 p) HV (n=8)		
			Substrate side	← →	Surface oxide
0	Non sealed	0 min	465	449	400
1	Hot water seal	15 min	450	450	300
		60 min	515	472	429
2	Medium temperature seal A	60 min	450	490	399
4	Medium temperature silicate seal	90 min	435	445	450
5	Organic sealer	Contact	458	460	416
6	Medium temperature seal B	50 min	454	469	450
7	Medium temperature seal C	50 min	469	458	454
8	High speed nickel acetate	25 min	425	410	430
9	Cold seal A	10/10 min	445	375	
		30/10 min	395	358	
		60/10 min	400	399	
10	Cold seal B	10/10 min	399	388	
		30/10 min	410	372	
		60/10 min	430	430	
11	Cold seal C	25 min	456	390	

Silicate Sealing

One of the possible mechanisms for silicate sealing is based on the formation of silica. The optimum ratio for soda-silicate should be around 1:3.3 (Na_2O : SiO_2). A typical procedure for silicate sealing is boiling the parts for approximately 30 minutes in a solution containing 5% sodium silicate. The effect of harness and wear resistance is reported to be minimal, mainly because no boehmite is formed.

Miscellaneous Sealing Methods

- Sealing by electrode position
- Fluoropolymers impregnation

The impregnation fluoropolymers, are called organic or impregnation sealing and leave non-wetting surface. The working temperature is about 30-40°C, the concentration is 15-30%, the pH is alkaline 8.5-9.00, the contact time is 30-40 sec, and dries at 75°C.

Experimental Method

Resin Coating

Chromate electro galvanizing aluminium was used as a substrate for resin coating. Chromate coating weight was 15-20 mg/m^2 and that of aluminium 10-15 m^2 . Resin was coated using a bar coater and then specimen was baked at moderate temperature using the cabinet type drying oven. The dry film thickness was adjusted by various size of bar coater.

Measurement of Physical Properties

Anti-finger printability was estimated by colour difference value (ΔE) between before and after Measurement of Physical Properties.

Anti-finger printability was estimated by colour difference value (ΔE) between before and after vaseline coating. Corrosion resistance was measured with plate specimens. Then corrosion test was performed with salt spray tester.

The dynamic friction coefficient was measured using a draw bead tester and calculated using the following equation.

$$\mu = \frac{Fd - Rd}{Fc \times \pi}$$

Fc = fixed bead clamping force
Fd = Fixed bead drawing force
Rd = roller bead drawing force

The test conditions was as follows:

-drawing speed: 500 mm/min
-bead radius: R 5.50

Interlaminar Resistance

To compare conductibility of organic coated aluminium, interlaminar resistance was measured.

We measured current value after making a firm contact of an electrode with specimen at a constant pressure.

Standard pressure: $2N/mm^2 \pm 5\%$
Experimental voltage: 1-2 V

Electric power: 0.5-15A

$R = A (1/I-1)$

Heat Resistance

Although silica improves corrosion resistance, it hampers formability of organic coated aluminium. To evaluate the effect of silica, the amount of additive silica in resin was varies without adding any other additive. The thickness of coating film was chosen as 3μm in order to minimize the effect of aluminium substrate.

Fig. 2 shows the effect of silica on friction coefficient. As the amount of silica increases, friction coefficient increases too. The result suggests that addition of silica would degrade formability. SO – S4 means the ratio of solid content of resin to silica and it varies form 0-20 phr.

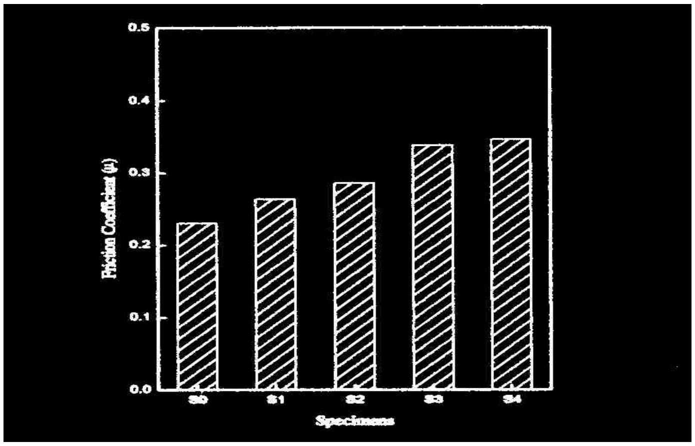

Figure 2 - Friction coefficient with silica content.

Without silica, red rust was observed all over the surface. However, in case of S4, white rust was observed only at limited area. This result means that silica in resin improves corrosion resistance of organic coated aluminium.

Fig. 3 shows ante-fingerprinting property of organic coated aluminium as a function of silica content.

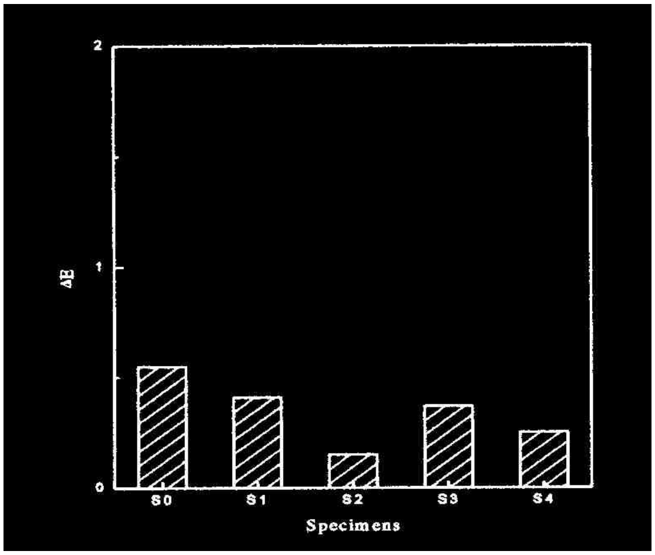

Figure 3 - Anti-finger property with silica content.

Since hydrophobic silica particles are evenly dispersed in organic coated aluminium regardless of silica content anti-fingerprinting property does not seem to be significantly affected by the amount of silica in resin. Surface morphology and Si mapping of samples confirmed the even distribution of silica.

Heat resistance Improvement

To improve heat resistance of organic coated aluminium sheet, the effect of heat resistant additives on heat resistance was scrutinized. Table 12 shows the variation of chemicals composition of solution by changing ratio of the base resin (A) to the heat resistant resin (B).

Table 12 - Composition Of Resin Solution

Item	Base Resin (A)	H.R. Resin B)	Hardener	Water
M1	15	141	2.52	18.21
M2	12	21	1.95	15.06
M3	9	37	1.25	9.07

Fig. 4 shows weight loss data of each resin with different chemical composition during TGA tests.

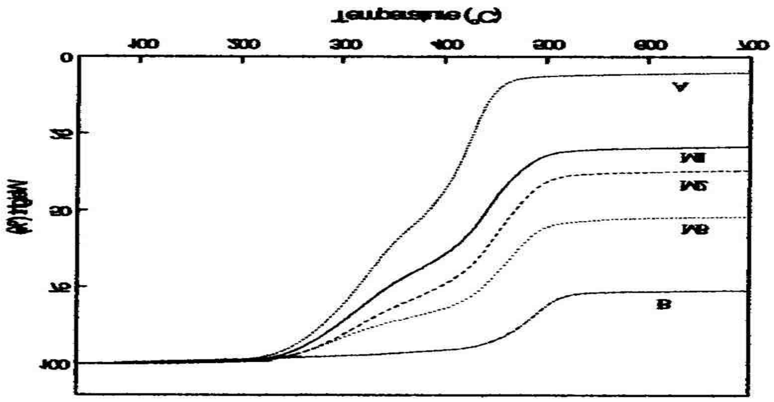

Figure 4 - TGA results for various resins

The results show that heat stability is superior at following order: B, M1, M2, M3, A. Heat stability of the heat resistant resin B is so superior to that of resin A that weight loss is only 16.5% up to 7000.

Fig. 5 shows variation of whiteness after exposing each sample with different solution composition at 1850.

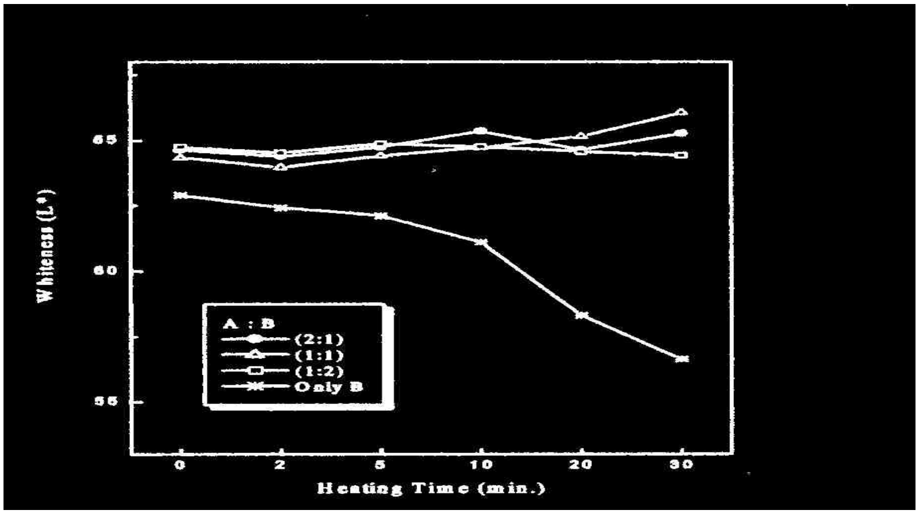

Fig 5 – Changes of whiteness for various resins

When adding heat resistant resin, no colour change was observed. However, base resin shows a sudden decrease in whiteness. Although the heat resistant resin improves heat resistance of organic coated aluminium sheet, with the heart resistant resin, white spots were observed on the

sample surface. Since white spot degrade the surface quality of organic coated aluminium, there should be a further study to develop a way to remove the white spots.
Variation of friction coefficient, as a function of the heat resistant resin is in Fig. 6.

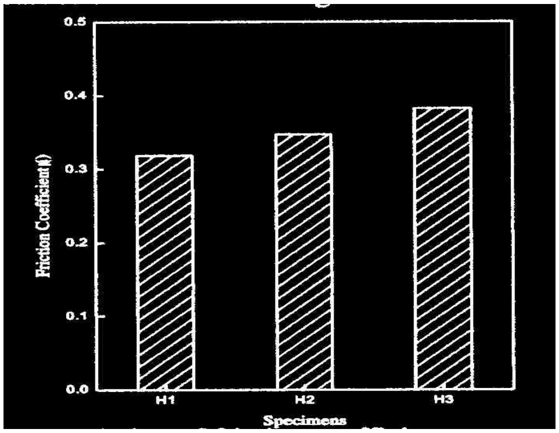

Figure 6 - Variation of friction coefficient.

Although friction coefficient of the sample with heat resistant resin is bigger than that of base resin, ratio of heat resin to the base resin does not affect significantly. The increase of friction coefficient seems to be related to the existence of silica, which is in the heat resistant resin.

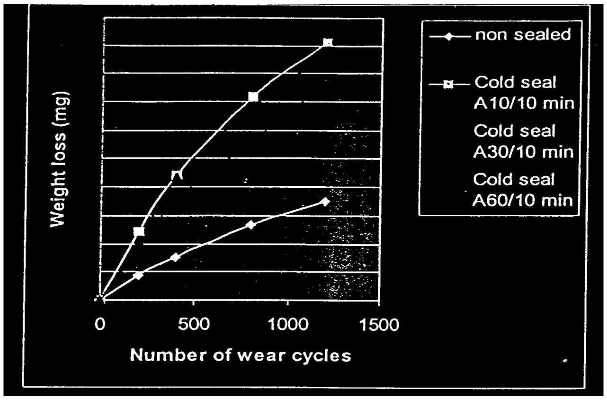

Figure 7 - Abrasive wear resistance cold sealed coatings, artificially aged

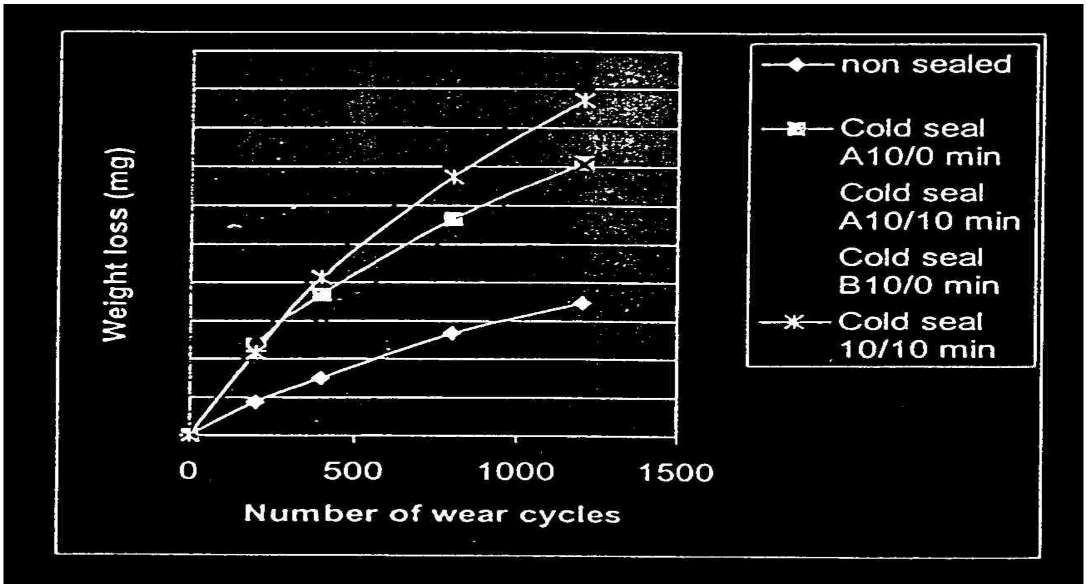

Figure 8 - Abrasive wear resistance cold sealed coatings with and without artificial ageing

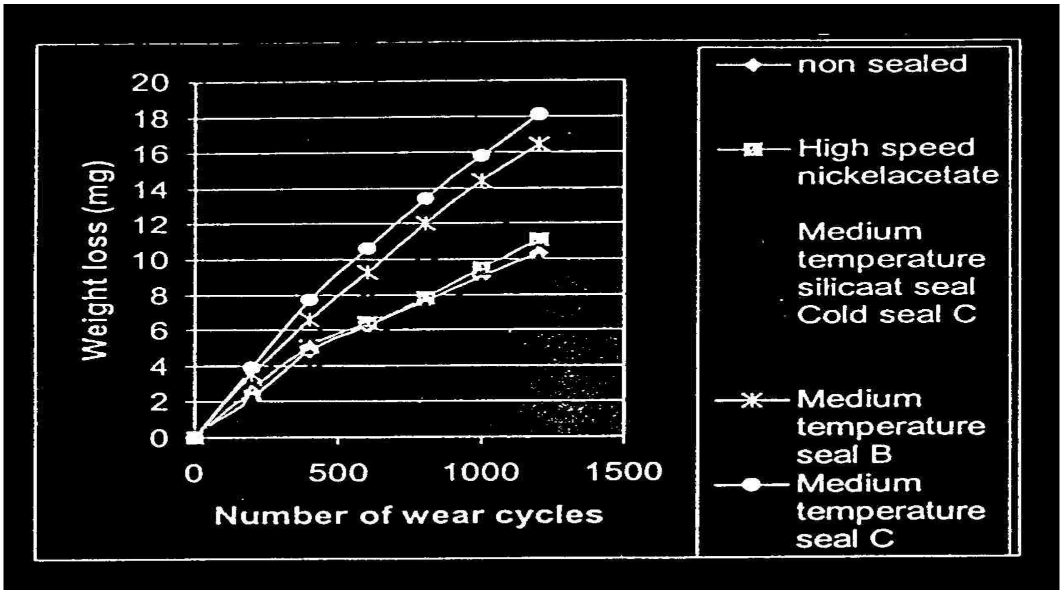

Figure. 9 - Abrasive wear resistance hard anodic coatings with different sealing methods.

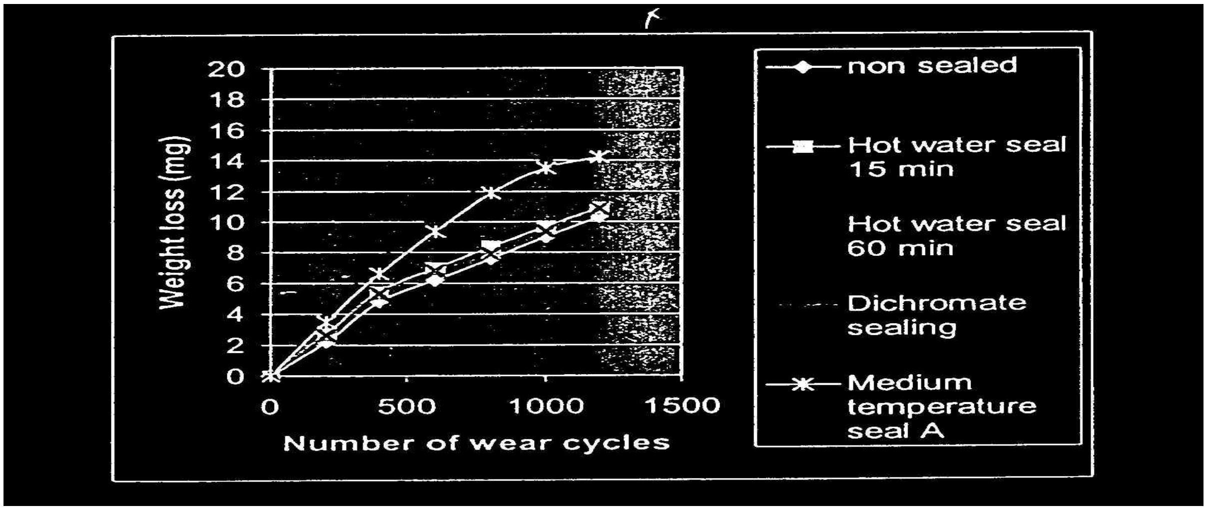

Figure 10 - Abrasive wear resistance hard anodic coatings with conventional sealing methods.

Metal Powder

During welding organic film layer is carbonised and as a result, there are problems of low longevity of welding electrode and poor surface appearance. To solve the above welding problems, we added metal powder to organic coating layer to lower electric resistance of organic film layer. The metal powders used were Fe, Ni, Cu, Zn, Sn, Fe-P and their size was about 1-8 µm. When adding metal powders, friction coefficient increased slightly. (Fig. 11)

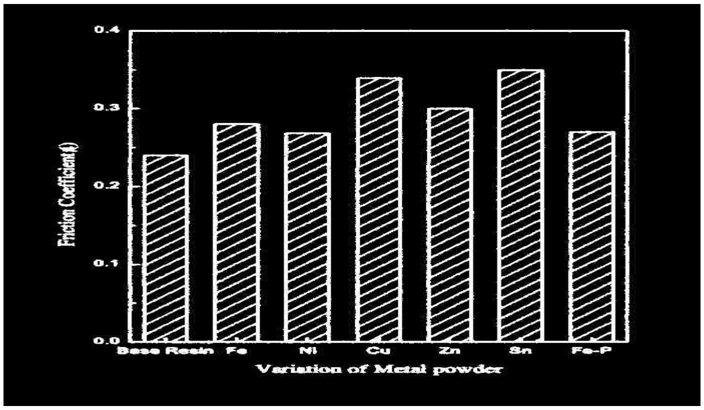

Figure 11 - Comparison of friction coefficient

This result suggests that metal powder seems to degrade formability of organic coated aluminium. Table 13 shows interlaminar resistance of coating layer with 10-25wt% metal powders. As metal powders were added, its interlaminar resistance decreased significantly. Therefore, addition of metal powder would improve weldability of organic coated aluminium.

Table 13 - Electric resistance of metal powder

Specimens	Current (A)	Resistance
Fe (10%)	0.99	0.50
Ni (10%)	0.98	0.04
Cu (10%)	0.89	0.50
Zn (10%)	0.72	4.20
Sn (10%)	0.80	2.50
Fe-P (10%)	0.96	0.03
Base resin	0.085	75.25

However, addition of metal powder makes solution unstable. That metal powder is settled at the bottom and solution becomes gel. Therefore, there should be found an appropriate solution to resolve the above problem if we want to use metal powder added to organic coated aluminium.

Conclusions

Hard Anodizing

1. The corrosion resistance was improved by the addition of silica, but silica does not help the lubricating action.

2. Addition of metal powder in resin gives a positive effect on the conductibility whereas it may degrade the resin solution stability.

3. Although addition of heat resistant resin has improved heat resistance or organic coated aluminium, it deteriorates surface appearance.

4. Knoop's hardness values are perfectly valid as shown in the comparative studies on cold and medium sealing.
5. Water sealing assures a correct Rcorr and good Rwaste.

6. Depending on the flouropolymers some can only coat the surface and some coat and penetrate into the surface.

Sealing

7. Cobalt and molybdenum sealing are perfectly valid and have less environmental impact than nickel, but they need further laboratory testing.

8. ISO 3210 tests are perfectly valid for cobalt/molybdenum.

9. Both sealed and unsealed films gain in weight with time. The weight gain is much greater for sealed than unsealed films-

10. A substantial increase in weight gain with ageing for nickel fluoride cold sealed finishes is due
11. to the nickel ion which has a catalytic effect on the hydration process, hence influencing the
12. results of the seal quality assessment.

13. The hydration reaction on samples treated in nickel fluoride cold seal solution is continuous.
14. The rate at which the hydration takes place depends on the temperature and humidity.

15. Low energy and chemical consumption.

16. Seal baths that are insensitive to contamination.

17. Sealed coatings that provide high resistance to crazing and weathering degradation and are

18. easy to clean and maintain

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