'Hard Anodizing for Aluminium Pieces -Supporting Friction and Wearing- For the Automotion and Motorcycling Industry (II)'

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This paper is the continuity of the research started in 2004 in the laboratory and the mechanical tests done in 2006. Part of this work was published and read in Sur/Fin 2007 (Cleveland, Ohio). In that first part, the results obtained with automotion and motorcycle parts were introduced. Silanes and polymers provides high resistance to parts against corrosion and minimum wear of parts in mechanical abrasion. This is done using directional vectors. The new aluminium and magnesium alloys are not going to be discussed now. After sealing in cold aluminium with flouride salts a second sealing is apply with a ramified silanes and polymers, thus gives the part great mechanical resistance against wearing. Reaction mechanism forms were observed between the aluminium-metal and the oxide resulting from hard anodizing. The interface occurring with silane and silane-oxide are free radicals of silicon and oxide-silicon, respectively. Afterwards, with the polymers reaction hexagonal closed structures are formed.

Key Words

Aluminium Alloys Silanes and polymers Impact minimization

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Figure 1 Microstructure of Anodic Film

Table 1 - Film Density Values

Al ₂ O ₃ fused ceramic	$3.8 - 4.0 \text{ g/cm}^{-3}$
α - Al ₂ O ₃ corundum	3.97
γ- Al ₂ O ₃	3.5
Al ₂ O ₃ .H ₂ O boehmite	3.014
Al ₂ O ₃ .H ₂ O bayerite	2.42 - 2.53
Thin barrier laver	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

Film Formation	$2\text{Al}+60\text{H}^{-} \rightarrow \text{Al}_2\text{OH}_3 + 3\text{H}_2\text{O} + 3\epsilon$
Film Dissolution	$Al \rightarrow Al^3 + 3\epsilon$
Oxygen evolution	$4OH \rightarrow H_2O + O_2 + 4\epsilon$
Sulphate oxidation	$2\mathrm{SO}_4^{2-} \rightarrow \mathrm{S}_2\mathrm{O}_8^{2-} + 2\varepsilon$

Table 2 - Anodic Reactions Of Anodizing

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).

Pure aluminium	50-55 VP
Aluminium alloys	60-140
Boehmite, Al ₂ O ₃ .H ₂ O	250-600
Pure aluminium Al ₂ O _{3:} sapphire corundum	1200 1800

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

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.

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	

Table 4 - Hard Anodic Films: Hardness Values

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
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- 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 incluye:

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

The fact however can be summarized as follows:

- Density values vary from 2.3 to 3.3. g/cm³, 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 $20-25^{\circ}$ C, 2-6 amp/dm² 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 \rightarrow 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.

Anodizing Conditions

All test panels are anodized in 18% sulphuric acid containing 5-7g/L dissolved aluminium. The tank volume es 3000 L and process temperature is $0^{\circ}\pm$ 5 coating thickness is 25 or 60µm.

Taber Wear Resistance

The abrasive wear resistance is measured as Taber resistance according to Taber Tester, model 6061 with two sets AA-5 abrasive wheels, from Taber Industries.

The panels were placed in a dessicator two hour before each weighting. The wear index is calculated from the weight loss after 10,000 wear cycles. A Type III coating is characterized by a maximum loss of 1.2 to 1.5 mg per 1,000 wear cycles if the copper content is less than 0.5%-2.0% maximum due to copper great contamination. A maximum weight loss of 2.5-4.0mg per 1,000 cycles is allowed for copper rich alloys.

The aluminium alloys of the 1,000 series passes the Taber test (**Table 1**) and the wear performance is independent of coating thickness.

Alloys from the 2000 series passes the Taber test when thickness is 25μ m. Increasing the tickness to 60μ m reduces the wear resistance and the coating do no pass the test criteria for a Type III coating.

Alloys from the 6000 series pass the Type III wear cruteruam but as thickness increases, the wear index increases. Increasing the thickness from 25 to 60μ m results en 72% higher wear index.

Only alloys from the 7000 series do not pass de Taber test. The alloy fails at low and hight coating thickness. However, the wear performance is independent of process time (~thinckness).

For the fous aluminium alloys investigated the 1000 series have the best taber performance. The wear performance for alloys form de 2000 and 6000 series decreases with encreasing thickness.

Compared to the average wear index (n=4), worst case scenario (maximum wear index out of four), the Taber wear index can be as high as $\pm/-50$ %. The deviation from the average value seems to be thickness and alloy dependent.

			Taber	r Wear Inde	x (mg/1,000 cy	cles		
	Thickness = 25µm				Thickness = 60µm			
Alloy	Ave	St.Dev.	Min.	Max	Ave (n=4)	St.Dev.	Min.	
	(n=4)						Max	
1100	0.40	0.10	0.10	0.60	0.49	0.25	0.40	0.60
2024	0.70	0.12	0.58	0.97	4.98	0.32	4.85	5.50
6061	0.58	0.31	0.19	0.99	1.15	0.15	1.20	1.40
7075	3.00	0.02	3.30	3.66	3.75	0.08	3.80	3.90

Table 5. Taber wear index for four aluminium alloys calculated
from weight loss after 10,000 wear cycles

Table 6. Reproducibility of the Taber Testing measured as the Wear Index on the front and the rear side of the test panels for the four alloys investigated

	Taber Wear Index (mg/1,000 cycles					
]	Thickness = 25	5μm	Th	ickness = 60µm	
Alloy	Front	Front Rear Diff. Front Rear I				
1100	0.42	1.20	0.78	0.35	2.20	1.85
2024	0.90	4.70	3.80	4.70	6.50	1.80
6061	0.98	1.65	0.67	1.10	1.60	0.50
7075	3.30	3.45	0.10	3.70	3.60	0.10

The accuracy of the Taber testing is shown in **Table 2.** Two panels of each alloy series show different wea characteristics from one side of the panels to the other.

Only one test panel out of the five meeting the test criteria of <1.2mg per 1.000 Cycles weight loss shown in Table 1 passed when Taber tested on the rear side. Only the 7000 series showed no change in Wear Index from the front of the rear side.

Acceptance values for abrasive testing according to ISO 10074 is alloy specific. The international standard contains 3 classes and 2 subclasses . Class 1 is alloys except those in class 2. Class 2 consists of two subclasses: Class 2a covers alloys of the 2000 series. Class 2b covers alloys of the 5000 series containing more than 1-2% magnesium and alloys of the 7000 series. Class 3b is all other casting.

According to ISO 10074, class 1 alloys are allowed to loose 1.2 to 1.5mg coating per 1.000 cycles. Acceptance criterio for class 2a and 2b are 4.0 and 3.5mg per 1,000 cycles. Alloy 1100 and 6061 passes the acceptance values- Alloy 2035 does pass if the coating thickness is low. Independenta of thickness alloy 7075 (class 2b) is the only alloy that does not meet the minimum requirement of ISO 10074.

Microhardness

The microhardness measured as the average of 7 indents for the investigated alloys (n=4) is shown in **Table 7**. Only alloy 2024 shows a decreasing microhardness with increasing thickness.

Alloy	Microhardness (HV _{0.010)} (n=4)			
	25µm	60µm		
1100	370 ± 15	370 ± 15		
2024	320 ± 15	280 ± 18		
6061	360 ± 17	360 ± 15		
7075	320 ± 15	310 ± 14		

Table7. Microhardness versus thickness

According to ISO 10074, only alloy 2024 (>250 HV_{0.05}) passes the criterio form microhardness. Minimum hardness for class 1 alloys is 400 HV_{0.05}. However, the microhardness shown in **Table 7** is measured using a load size of 8-12g.



Figure 2 - Simplistic mechanism of cros-linking between metal and polymer





Table 8 – Silane Chemistry

	SILANE CHEMISTRY
BTSE	(C ₂ H ₅ O) ₃ -Si-CH ₂ CH ₂ -Si-(OC ₂ H ₅) ₃
VS	H ₂ C=CH-Si-(OC ₂ H ₅) ₃
γ-UPS	H_2N -CO-NH-C H_2 -C H_2 -C H_2 -Si-(OC ₂ H_5) ₃
γ-APS	H ₂ N-CH ₂ -CH ₂ -CH ₂ -Si-(OC ₂ H ₅) ₃
A-1170	(C ₂ H ₅ O) ₃ -Si-CH ₂ CH ₂ -CH ₂ -NH-CH ₂ CH ₂ -CH ₂ -Si-(OC ₂ H ₅) ₃
A-1289	(C ₂ H ₅ O) ₃ -Si-CH ₂ CH ₂ -CH ₂ -S ₄ -CH ₂ CH ₂ -CH ₂ -Si-(OC ₂ H ₅) ₃
SAAPS	H ₂ C=CH-C ₄ H ₄ -CH ₂ -NH-CH ₂ -CH ₂ -NH-(CH ₂) ₃ -Si-(OCH ₃) ₃ .HCI

Table 9 - Successful Application of Silane Treatments on Painted Systems

WHERE DO SILANE TREATMENTS WORK			
Painted Systems:			
•	Painted cold-rolled steeel		
•	Galvalume coil paint lines		
•	Painted hot-dip galvanized steel		
•	Cast aluminium wheels		
•	Coated aluminium beverage cans		

Table 10 - Successful Application of Silane Treatments on Unpainted Systems

WHERE DO SILANE TREATMENTS WORK ?
Unpainted Systems:
• White rust inhibition of hot-dip galvanized steel
• Al 2024 aircraft alloys
• Weathering of TiZn roofing sheets

ADVANTAGES OF NEW SILANE TREATMENTS
Optimised for the metal and application
Environmentally compliant
Corrosion performance superior to chromate and phosphate
Corrosion resistance even without paint
• Fewer steps than phosphating

Table 11 - Advantages Of New Silane Treatments

Hard Anodizing and Integral Colour Anodizing

Hard anodizing is practically popular for engineering purposes. A thickerfilm 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. I appears there exists a colouring voltage when 4DC is ised, while in the case of modulated current, event the anode voltage (cathodic polarization being negligible, the peak or surge voltage may happen to be 30 V). Thus coloroured 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 ate ina 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.

Organiz 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 eradication on the film. As it may be clear now that chromic acid film constains ca. 3% Cr₂O₃, oxalic acid film ca. 3 % oxalate and sulphuric acid ca. 14 % shulp.hate and hasd sulphuric acid coating, intergral colour coating contain Al and some shulp.hate. Therefore, integral colour coating electrolytes operation at 25-28°C, without strong cooling, may replace sulphuriic acid hard coating below 10°C. The colour of oxalic acid film comes from another origin. Carboxulate oms 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 coworkers, complying with the needs of hard, smooth, lustrous and high electric breakdown voltage form the EEC advanced electronich industry. A unique and creative designing in bath construction, cathode locations, racking and improvement of anode throw and way of cooling an clearing at least 5000 V/100 micron or more and Hv above 450°C. The operation condicions and film properties are quite different.

• Electrolyte:

- Oxalic acid 80 g/l
- Formic acid 80 g/l
- Counter cathode:
 - Graphite
- Temperature:
 - $5-40^{\circ}$ C C.D. $2-6a/dm^2$, 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 precipates 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.

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/dm^2 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 $alpha-Al_2O_3$ (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. Demostrated a possible pretreatment to improve stresscraking 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.

CONCLUSIONS

- 1. It is generally accepted microhardness is a measure of wear performance of coatings. National and International Standards specify acceptance criteria for both wear resistance and microhardness.
- 2. The wear indexes presented in this paper shows a correlation between microhardness and wear resistance is alloy specific and dependent on the test method. Both Taber and ISO 8251 testing on alloy 2024 shows reduced wear performance with increasing thickness.
- 3. The reduced performance is correlated with reduced microhardness. However, Taber testing of 6061 alloy shows reduced wear performance with increasing thickness, even tough the microhardness is independent on thickness.
- 4. With increasing thickness, ISO 8251 testing identified a reduced initial wear and a constant post wear. If the post Wear, which is influenced by the compactness and composition of the oxide coating, is independent of thickness, so should the microhardness.
- 5. The result presented in this paper show that reproducibility of wear performance according to ISO 8251 is better than Taber testing (5% compared to 60%). Furthermore, it can not be recommended to do Taber testing on both sides of a test panel.
- 6. Corundum and rubi films are very hard. There are comparable to hard anodizing but they have inferior chemical and physical propieties.
- 7. Hard anodized and integral colour parts for automotion and motorcycle have high resistance to corrosion, wear and mechanical abrasion.

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