Improvement of printing quality of aluminium substrate

St. Theohari, P. Gioti, I. Iakovidis,
A. Tsigonias, and I. Sianoudis

IC
Leipzig 2016

48th Conference of the International Circle
of Educational Institutes for Graphic Arts
Technology and Management

29 May to 2 June 2016

Introduction

- Aluminium is a lightweighting, long-lasting, modern and recyclable material that ensures contemporary aesthetic, durability, lightfastness and resistance against chemicals with multiple applications in various fields.
- Aluminium has gain a great interest in the field of graphic arts for special or external applications (panels, signage, barcodes, awards, labels, etc.) due to its extensive highly decorative and fashionable design appearance.

- Among various processes that applied on aluminium surface in order to render it printable, the most effective is an electrochemical treatment named "*anodizing*".
- A thin, porous, uniform, colourless, transparent and protective film is formed on aluminium substrate.
- The influence of treatment parameters on print quality and properties of the imprint is mentioned only in a few patents and commercial references.

The process

- During anodizing a current passes through the electrolyte and the negatively charged anions migrate to the anode (aluminium), where they are discharged with a loss of one or more of their electrons.
- In an aqueous solution oxygen unites chemically with the aluminium and the result of the reaction depends on a number of factors, particularly the nature of the electrolyte, the consequent reaction products which are formed, and the operating conditions such as current potential, bath temperature and time of treatment.

$$Al^{3+} + O^{2-} \rightarrow Al_2O_3$$

- In certain cases the reaction products may be sparingly soluble in the electrolyte and form a strongly adherent film, which is non-conducting when dry, over the anode.
- Film growth takes place and the process is accompanied by localized dissolution of the film.
- Subsequently pores are formed in the coating, which are wide enough to allow continuing access of the current to the metal.

The anodic oxide films

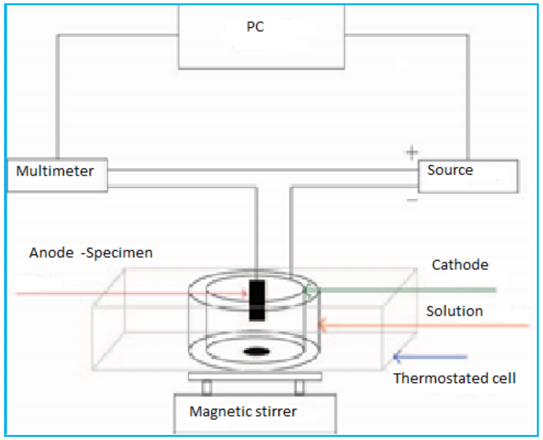
- The porous nature of the anodic oxide films allows the production of coloured coatings by deposition of organic dyestuffs or metallic pigments; thus a wide range of decorative and protective finishes are possible.
- The coatings obtained by anodizing are not only superior mechanically, but can also be produced with much higher corrosion and abrasion resistance.

Aim of the study

- The aim of the present study was to investigate the influence of certain anodizing parameters on print quality of anodized aluminium specimens.
- The influence of temperature, of the type and concentration of electrolyte, and of applied voltage on the characteristics of oxide layer (thickness, roughness - porosity, pores diameter, and morphology) and thus on colour parameters, lightfastness and adhesion of specimens were studied.

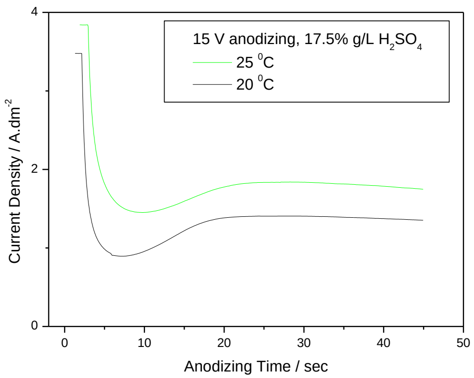
Experimental procedure

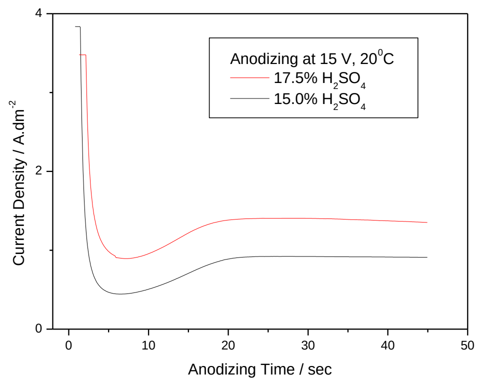
Pretreatments

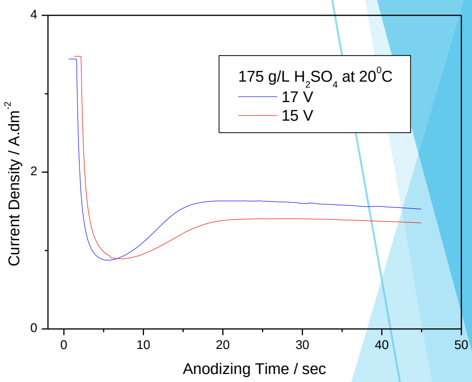
- Specimens of AA1050 aluminium alloy were degreased in acetone, etched for 1 min in a solution containing 40 g/l NaOH at 40ºC, rinsed in deionized water and immersed for 1 min in 1:1 v/v HNO_3 at room temperature.
- After rinsing in deionized water and drying in a cool air stream, the specimens were stored in a desiccator.
- Anodizing was carried out via a Delta Electronika Power Supply SM3004-D, at a constant voltage 15V (or 17V) in 1.8M H_2SO_4 (S.A.) for 40 min or at 30 V in 0.4M H_3PO_4 (P.A.) for 5 min at various temperatures.
- 

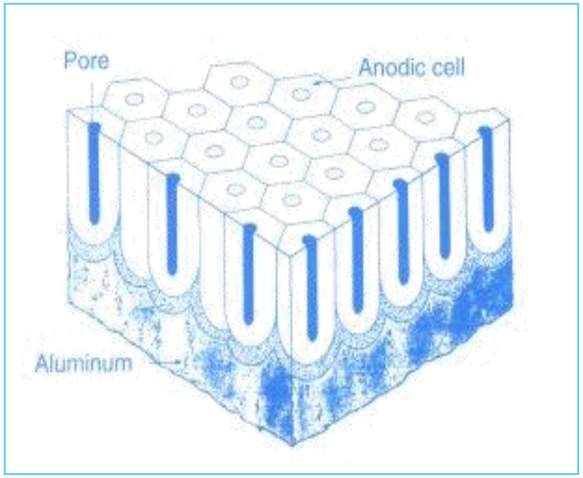
Anodizing

- Current transients during anodizing were recorded via a multimeter (Keithley 2000) connected with a PC and the thickness of oxide layer films was measured by a Permascope EC8 (Fischer Technology, Inc. Norwalk).







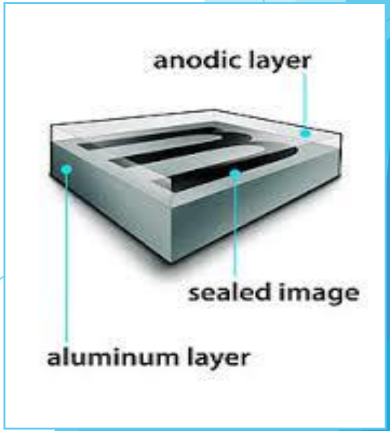


Printing

- Anodized specimens were printed by screen printing with epoxy-catalytic inks or by inkjet printing with UV curing inks and then sealed in boiling, deionized water.





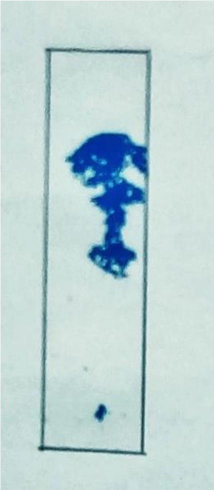
Colour and reflectance measurements

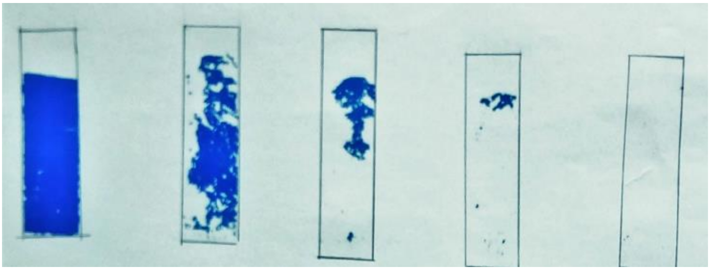
- Reflectance of printed specimens was measured by a Spectrometer Ocean Optics (model HR-2000 with optical fiber, Integrating Sphere, 50 mm, with glass trap, ISP-50-8-R-GT Micropack). Measurements were carried out via calibration with a standard Spectralon reflectance probe).

- Colour and print density measurements were carried out by a Spectrophotometer SpectroEye, GretagMacbeth.

Chemical resistance, adhesion and lightfastness

- Printed specimens were tested against common chemical solvents (water, acetone, ethanol)
- They were evaluated according to ASTM D3359 (Measuring Adhesion by tape test)
- and ASTM D3424 (Lightfastness evaluating).





Microscopy

- Surface images of printed specimens obtained by an optical stereo-microscope Olympus 5261 10X-80X connected with a camera Sony Ex Wave HAD and PVR Plus software.
- Observation and analysis were carrid out by a Scanning Electron Microscopy JEOL JSM-6510 LV - EDAX (Oxford Instruments, 10mm^2 Silicon Drift Detector - x – act).

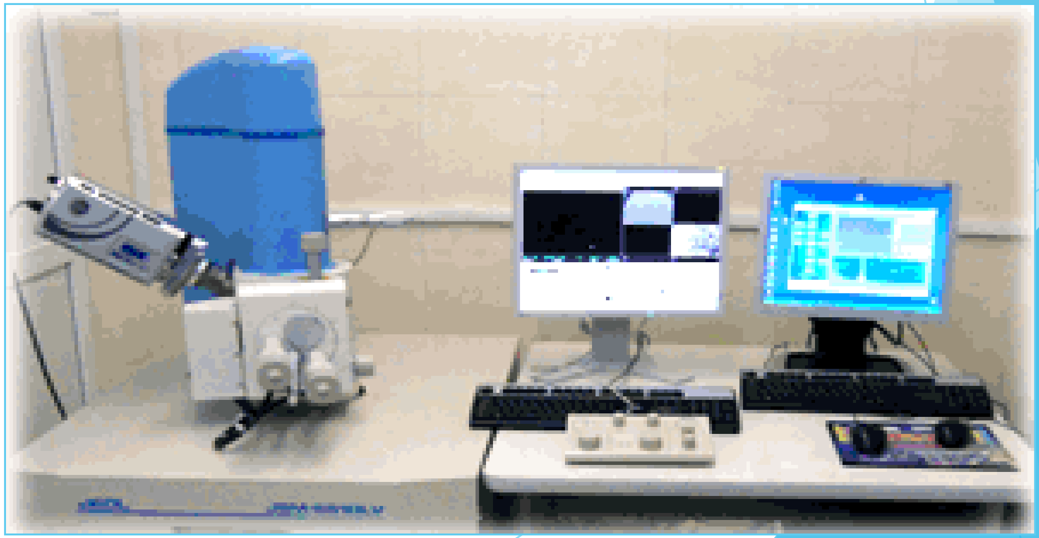


Image analysis

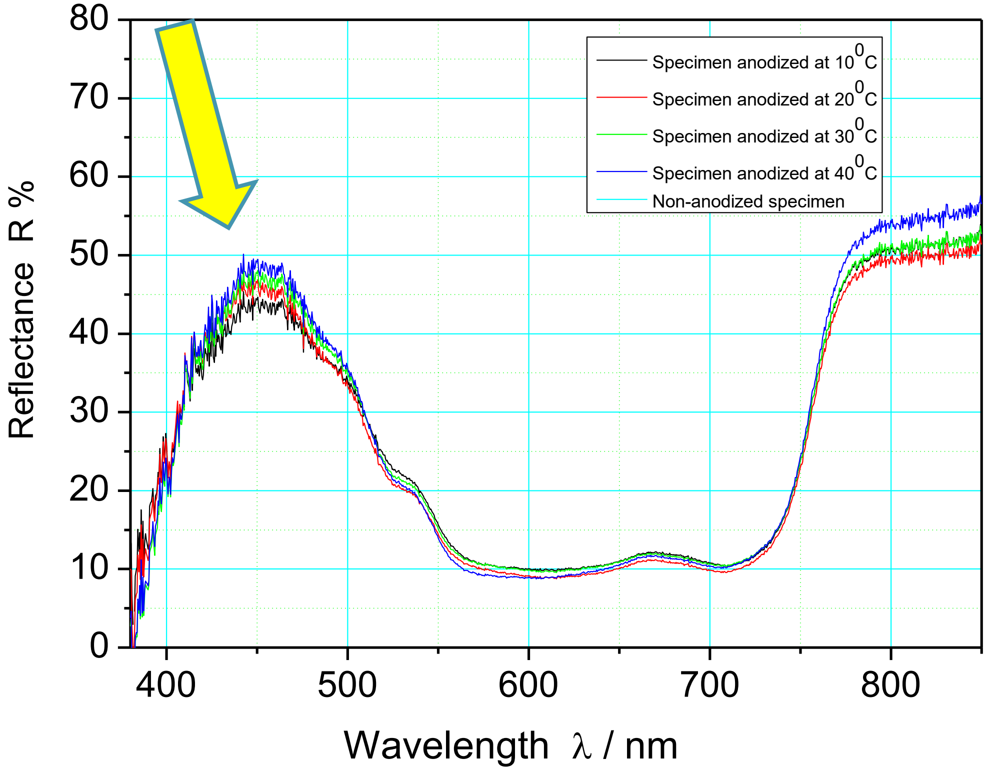
- In order to obtain quantitative information on the results of adhesion test on printed surface of the specimens, image analysis was performed by using the ImageJ 1.50b software.
- The micrographs were at first transformed to a suitable format, whereupon particle analysis was applied for the estimation of the percentage (%) of the removed printed surface area of the specimens by the tape test.
- Print quality of the specimens was evaluated by the same method.

Results and discussion

- Initial experiments
- Part I
- Part II
- Part III

- The reflectance spectra of specimens anodized in P.A. at various anodizing temperatures and printed by digital (inkjet) printing are presented in Fig. 1

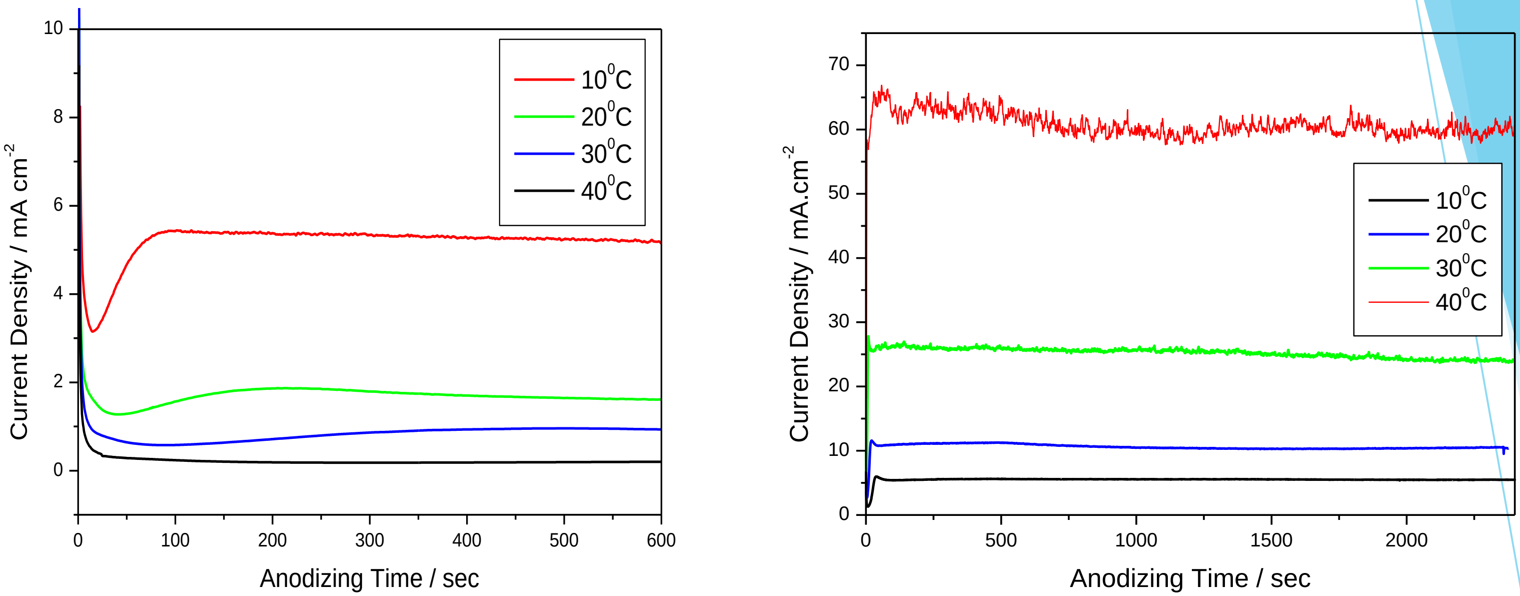
1. λ_{max} values lie in the region of 450 nm (blues region), which is consistent with the experimentally used blue ink.
2. The curves show similar shapes, but slight differences that indicate slight differences in the structure (porosity and roughness of the surface) due to the different anodizing temperatures.



- ***Fig. 1****. Reflectance spectra (R%) of digital printed specimens of anodized aluminium in P.A. in the range of 380-730 nm*

- The observed λ_{max} values are in the region of about 450 nm, which lies in blues region and is consistent with the experimentally used blue ink.
- It is also observed that while all these curves show similar shapes, they appear slight differences in absolute values of R% that may indicate slight differences in the structure, porosity and roughness of the surface of films formed at various anodizing temperatures.
- It is referred that the optical properties and the reflected colour of an anodic aluminium oxide film can be modified by adjusting its thickness by varying the anodizing conditions.

- The investigation of the influence of the anodizing conditions on the printability and print quality of anodized aluminium specimens, as well as on their colour parameters CIE_{Lab} and print density (D_{CMYK}) values was of great importance.
- The above results were related with the theoretical models of the structure of the anodic oxide films, which are formed by anodization in two different acidic solutions (P.A. and S.A.) at various temperatures.

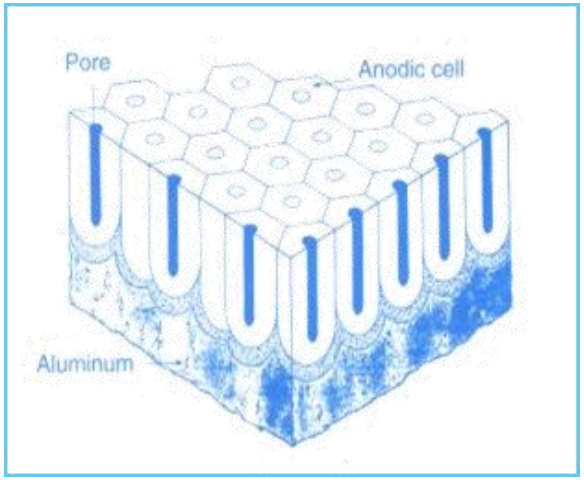


a b

Fig. 2a,b*. Current density-time responses during anodizing of AA1050 specimens in P.A. (a) and S.A. (b) at various temperatures*

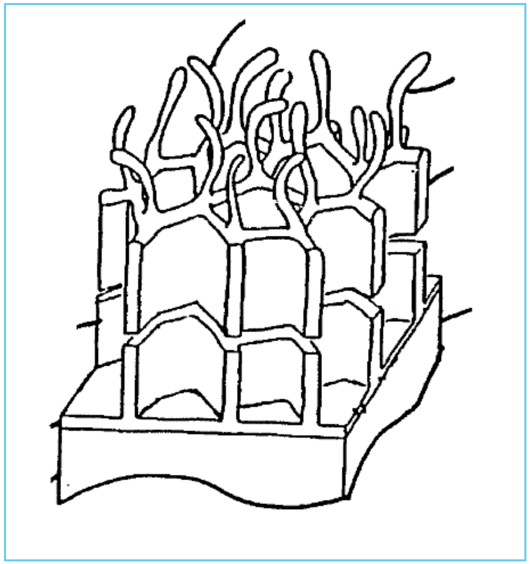
Differences between the current-time responses during anodizing at various temperatures in two different types of electrolytes

- In the case of **sulphuric acid solution**, the film consists of two layers, a porous thick outer layer with hexagonally shaped cells with a central pore perpendicular to the metal surface and an inner barrier layer, which is very thin, dense and dielectrically compact, present between the metal and the porous layer.

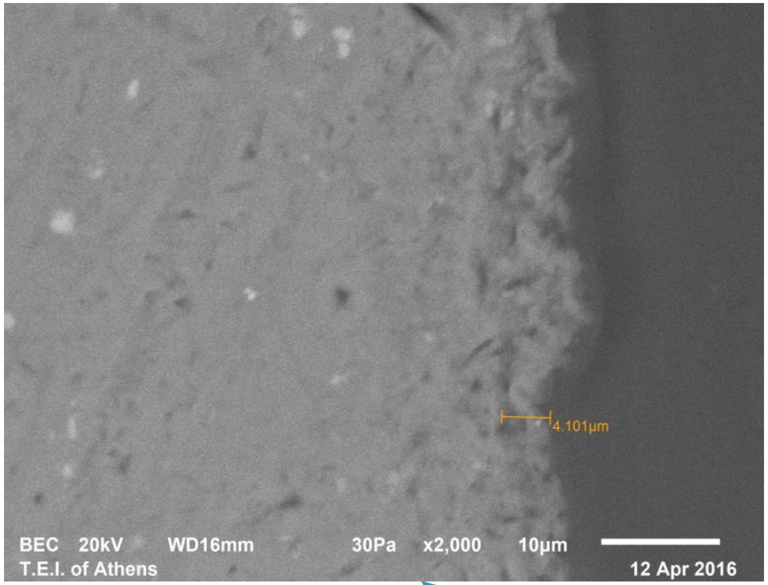


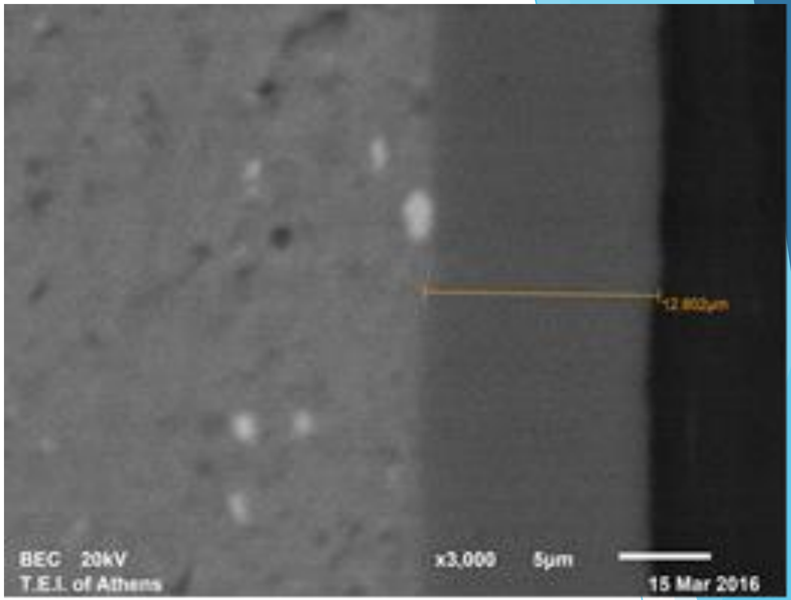
- These coatings are thick (5-35 μm) and if sealed subsequent to anodizing, give very good corrosion resistance as well as being harder and more wear resistant.

- On the other hand, the anodic films produced in **phosphoric acid** are very thin (about 3-5 μm) and show large pore diameter; some researchers describe these films with oxide whiskers or protrusions on their surface; it is mentioned that this morphology interlocks with dyes, inks or adhesives.



- One of its most widespread uses is the preparation of lithographic plates for printing purposes.





4,1 μm

12,8 μm

a

b

Fig. 3a,b. *Cross-section SEM images of anodic films formed on AA5052 specimens in P.A. (a) or S.A. (b) at 20 ° C.*

Differences between the resultant anodic oxide films formed in P.A. and S.A.

Part I

- The role of the temperature on print quality of specimens anodized in **phosphoric acid (P.A.)** was investigated.
- Anodized specimens were printed by two methods: digital printing with UV curing ink or with epoxy-based inks by screen print.
- Colour parameters CIE L*, a*, b*, results of adhesion tests and images of printed specimens are presented in Tables 1, 2 and Figures 4, 5.

***Table 1**. The influence of anodizing temperature on colour parameters CIE_{Lab} of screen printed specimens and D_{CMYK} of digital printed specimens of anodized aluminium in P.A.*

	Screen Printing				Digital Printing			
Anodizing temperature in P.A.	**CIE $_L$***	**a***	**-b***		**D_C**	**D_M**	**D_Y**	**D_K**
10˚C	7,37	8,59	30,25		2,12	2,45	1,95	1,22
20˚C	7,38	8,78	30,44		2,24	2,50	2,07	1,33
30˚C	7,58	8,38	30,84		2,19	2,54	2,01	1,29
40˚C	8,03	8,27	29,31		2,06	2,50	2,10	1,20

A rather stable printability and no significant differences are observed by naked eye

- As seen in table1, the values of CIE_{Lab} and print density (D_{CMYK}) of digital – inkjet specimens showed a rather stable printability for specimens anodized at various anodizing temperatures.
- It is obvious, that the differences for specimens printed by screen printing are not visible clearly by naked eye (ΔE 0,27 – 0,60 – 1,4 respectively for specimens anodized at 10ºC, 30ºC and 40ºC compared with the specimen that anodized at room temperature (20ºC).
- ΔE* color difference was calculated from equation (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

- ***Table 2***. *Printed area removed (R.A.%) from printed specimens anodized at various temperatures in P.A. after adhesion tape test (D3359 ASTM classification is given in parenthesis)*

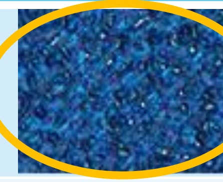
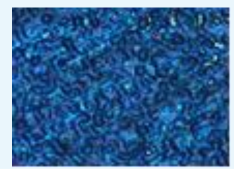
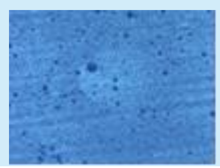
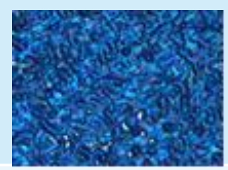
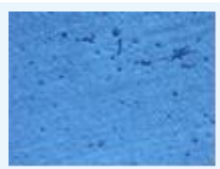
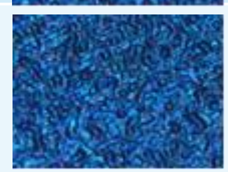
Anodizing T (°C)	R.A. % Screen printing	R.A. % UV Inkjet printing
Non-anodized	89.0 (0B)	
10 °C	0.3 (4B)	60.0 (1B)
20 °C	0.3 (4B)	14.9 (3B)
30 °C	0.2 (4B)	2.7 (4B)
40 °C	1.0 (4B)	0.2 (4B)

1. Excellent adhesion for specimens printed by screen print until 40◦C
2. Gradual improvement in the case of inkjet printing as temperature increases due to the different modification and the enhanced porosity of the substrate

- The above results indicate that anodized specimens and printed by screen printing appeared excellent adhesion.
- However, the aluminium specimen anodized in P.A. at 40^{o}C appeared to be slightly affected (1% removed area) probably due to the elevated temperature.
- On the other hand, it is obvious that there is a significant improvement of adhesion with temperature (and especially at 30-40°C) in the case of inkjet print method.

- This fact is indicative of the different modification of the structure of the anodic films influenced by the temperature, since they obtain wide and open pores and permit UV curing ink to be linked more effectively with the substrate.
- Elevated temperatures cause increased current densities and subsequently electric charges that pass during anodizing, and due to the thermal field assisted dissolution, they enhance the coating porosity and the dissolution of the outer oxide surface.

- ***Fig. 4*** *The images (X50) from the optical microscope of anodized (in P.A.) aluminium specimens printed by two different inks and screen and inkjet print methods.*

Anodizing in P.A.	Screen print (X50)	Inkjet UV (X50, X200)
Without anodizing		
10°C		
20°C		
30°C		
40°C		

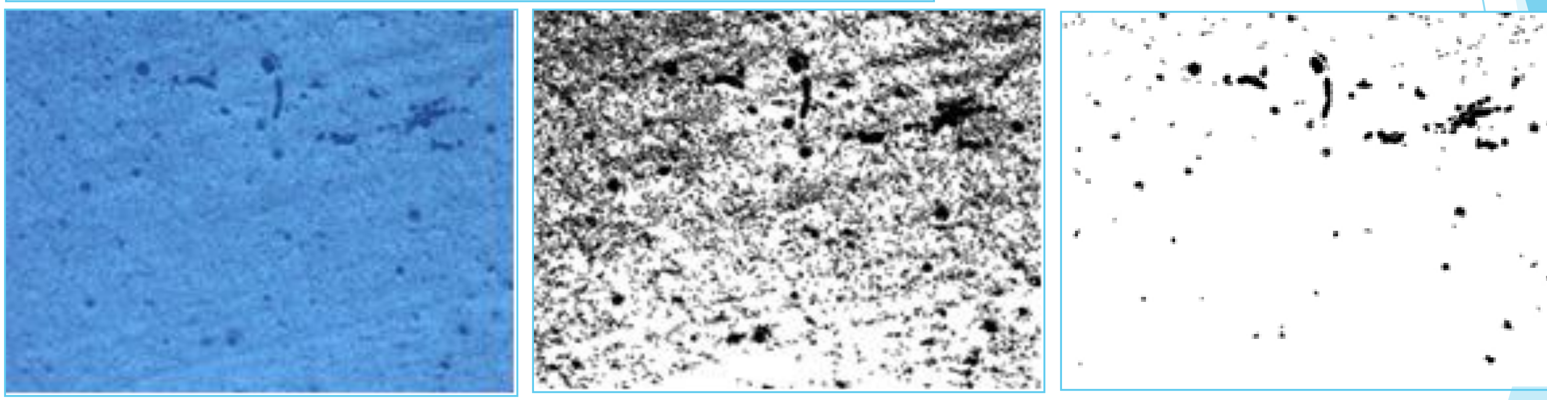
1. Excellent printability of anodized specimens due to the porous substrate that allows a better ink-film formation (10-30◦C)
2. Some uncovered areas and non-uniformities in the case of digital printed specimen at 40◦C

- Figure 4 confirms that the anodized specimens showed a very good printability in comparison with a non-anodized one, which appears non-uniformities of the ink layer film for both printing methods and some uncovered areas (digital printed).
- These results are in accordance with the previous ones related with the colour parameters, and indicate that anodized specimens appear good printability in all cases, due to the fact that the anodic oxides formed in phosphoric acid have an extremely porous and absorptive character.
- The results also indicate a slight improvement especially when anodized at temperature range of 10^{o}C-30^{o}C, for both inks and methods of printing, confirming that anodic oxide films appear morphology suitable to accept the ink and form a uniform layer, as the images show.
- However, the digital printed specimen that has been anodized at 40^{o}C shows some discontinuities and uncovered areas and indicates that anodizing at elevated temperatures favours dissolution of the film and possible phenomena of spongy and powdery oxide film modification that affects print quality. The image shows a less uniform ink layer, with some uncovered sites, and a morphology similar to that of non-anodized specimen.

- Image analysis was performed in order to obtain quantitative information on the results of quality of printed surface of the specimens. (**Fig.5 a,b,c**).

Local ink aggregates (2.5-3.8 spots/mm^2) only 1.4 spots/mm^2 on the specimen that anodized at 30°C

Average diameter of spots 0.12mm



In all cases 2.6-3.6% of printed area was covered by aggregates only 2.3% on specimen anodized at 30°C

- It is concluded that P.A. gave the best results at slightly above room anodizing temperatures (20-30°C).

Part II

- The influence of anodizing temperature of another type of electrolyte - **sulphuric acid solution (S.A.)-,** on print quality of anodized specimens was studied.
- The anodized specimens were printed with UV curing ink by digital printing.
- The print density values (D_{CMYK}) and the results of adhesion tests of the specimens are presented in Table 3 and 4.
- Their photographs from the optical microscope (X50 and X200) are presented in Fig. 6.

- ***Table 3***. *The influence of anodizing temperature on print density (DCMYK) of digital- inkjet printed specimens of anodized aluminium in S.A.*

Anodizing temperature in S.A.	D_C	D_M	D_Y	D_K
10°C	2,57	2,09	1,45	2,28
20°C	2,55	2,08	1,41	2,27
30°C	2,76	2,11	1,65	2,46
40°C	2,68	2,05	1,55	2,34

Good printability and performance of printed specimens
A slight improvement of colour parameters with temperature

- From these results (table 3), it is obvious that
- a) anodized specimens show a good printability and performance in all cases and
- b) as the temperature of anodizing solution increases, the values of colour parameters become higher, due to the modification of the film.
- The substrate seems to keep a larger amount of ink (for the screen printed specimen anodized at 40◦C in Table 3), but it is not really able to form a uniform ink layer with good performance on the surface, as seen in the next slides.

- ***Table 4****. Printed area removed (R.A.%) from printed specimens anodized at different temperatures in S.A. after adhesion tape test (D3359 ASTM classification is given in parenthesis)*

Anodizing T (°C) in S.A.	R.A. % UV Inkjet print
Non-anodized	100.0 (0B)
10°C	91.1 (0B)
20°C	90.1 (0B)
30°C	2.3 (4B)
40°C	0.0 (5B)

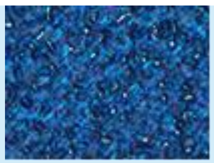
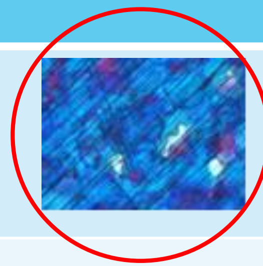
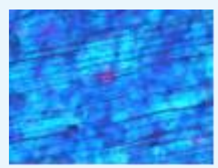
The results show that the anodic films show a gradual improvement as the anodizing temperature increases and especially at 30°C and 40°C. They confirm that as the temperature increases the modification of the structure of aluminium surface obtain more widen and open pores that permit the ink to be linked with the substrate.

- The results confirm an important improvement due to the modification of the structure of the anodic films, and the more widen and open pores that permit UV curing ink to be linked with the substrate as the temperature increases.

- In the case of digital printing with UV inks the best results derive from anodizing in S.A. at temperatures 30-40°C.

Fig. 6. *Optical photographs (X50 and X200) of surface morphology of printed by digital-inkjet printing specimens of anodized aluminium in S.A. at various temperatures.*

Specimens printed at 40◦C are similar to the non-anodized ones, and appear uncovered areas and non-uniformities probably because of the “affected” substrate at this temperature

Inkjet UV X50	X200	Anodizing Temperature in S.A.
		Without anodizing
		10°C
		20°C
		30°C
		40°C

The best results derive at 30°C in the case of digital printing.

These findings are in good agreement with those obtained in the P.A. electrolyte (Part I).

- Although results related with colour parameters seemed to be better for the screen printed specimen anodized at 40◦C (Table 3), the micrographs (Fig. 6) indicate the existence of defects and possible break down phenomena in the anodic oxide film.

- They confirm that in conditions favouring film dissolution, the oxide film may suffer by attack by the end of anodizing process, since the printed specimen that has been anodized at 40°C is rather similar to the non- anodized one (some white, discontinuities and uncovered areas are observed).

- Regarding results in Tables 3,4 and Fig.6 it is observed that the best results derive from anodizing in S.A. at temperatures about 30°C in the case of digital printing with UV inks.

Part III

- The **part III** of the study deals with the investigation of the role of concentration of electrolyte (a), voltage (b) and anodizing temperature (c) in the range of 20-25°C.

- The results are presented in Fig. 7 a,b,c and 8.

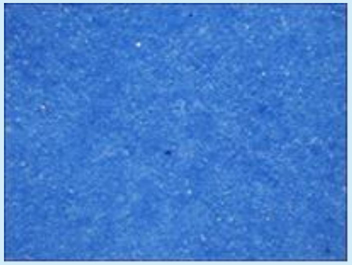
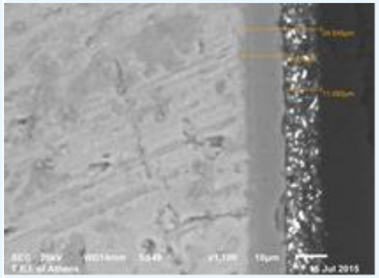
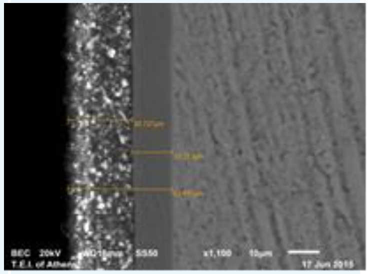
Specimen- Anodizing conditions	A- 1.5M S.A. 15V, 20°C	B- 1.8M S.A. 15V, 20°C
Optical photographs (X30)		
SEM cross-sectional micrographs		

Fig.7a

(a)

- Increasing the concentration of electrolyte causes increase in current density and higher solubility of the oxide film, which is responsible for the increase of the pore diameter and the coating porosity of the film.
- A thicker ink film layer is formed on specimen B (20,7 μm) while ink performance is better than that on the specimen A (11,1 μm).
- Increasing the concentration of S.A. results in an improvement of CIE a*, b*, measured values (ΔE 2,9).

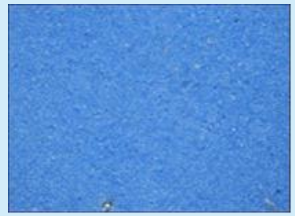
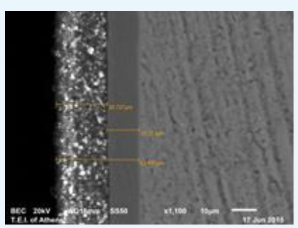
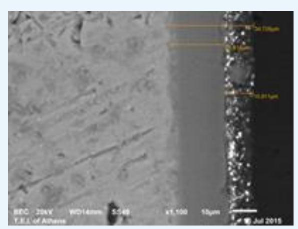
Specimen-Anodizing conditions	B- 1.8M S.A. 15V, 20°C	D- 1.8M S.A. 17V, 20°C
Optical photographs (X30)		
SEM cross-sectional micrographs		

Fig. 7b

(b)

- Increasing the anodizing voltage causes decrease of porosity of the anodic film that probably prevents the substrate to keep and interlock the ink layer in a sufficient extent.
- Thus a decreased thickness of ink layer is formed on specimen D (10,9 μm of ink layer on D) in comparison with that on specimen B (20,7 μm of ink layer on B).
- A slight increase in the anodizing voltage causes decrease of measured values of CIE a*, b* (ΔE 7,1).

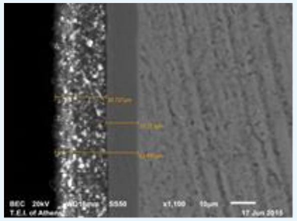
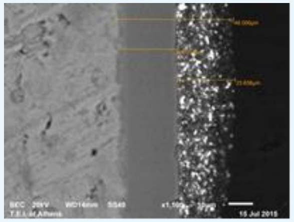
Specimen- Anodizing conditions	B- 1.8M S.A. 15V, 20°C	C- 1.8M S.A. 15V, 25°C
Optical photographs (X30)		
SEM cross-sectional micrographs		

Fig. 7c

(c)

- A slight elevated temperature of the electrolyte causes an increased current density and enhance the coating porosity due to the thermal field assisted dissolution and the dissolution of the outer oxide surface.
- A slight thicker ink layer is formed on specimen C (23,6 μm of ink layer) in comparison with specimen B (20,7 μm of ink layer).
- A slight increase of the anodizing temperature in S.A. solution cause a slight increase of the values of CIE a*, b* (and ΔE 4,3).

- However, photographs (X30) of the surface of a printed specimen anodized at 25◦C showed the initiation of some defects and imperfections, like pits on the surface of the specimen indicating that increasing anodizing temperature not only enhances the printability of the surface but also the initiation of problems.

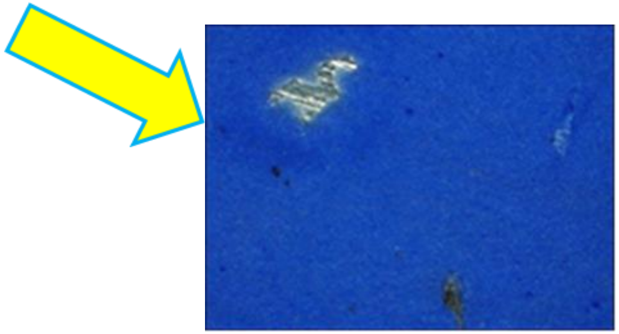


Fig.8

- It is very important to mention that all the above specimens (A, B, C, D) gave **excellent adhesion tape test results** (with the exception of specimens C and D that appeared <5,0% removed area).
- They also showed **excellent Lightfastness and fastness against common chemical solvents** (water, ethanol, acetone) indicating that the suggested method is an excellent pretreatment for aluminium surface prior to printing by these methods for external applications.

Concluding Remarks

- The study confirmed that the suggested method of anodizing of aluminium substrate treatment enhances adhesion of ink and lightfastness properties of printed specimens; especially, varying the anodizing conditions may improve print density, lightfastness and adhesion of the specimens.
- A further investigation of the influence of the above conditions on print quality may clarify the optimum conditions of printing by various methods.
- This investigation would be of great academic and commercial interest, whenever special applications or excellent adhesion, resistance properties and quality of printed substrates are required.

(http://www.primodize.com/gsm/barcodes/)

(http://www.altechanodizing.com/anodizing/)

Author biography

- ***Dr. Stamatina Theohari*** *holds a B.S. and a PhD in Chemistry (University of Athens, Greece).*
- *Her research involves surface treatment of materials and printing substrates, pigments, dyes, printing inks and coatings.*
- *She is Assist. Professor and Academic Coordinator for Erasmus+ Programms of Technology of Graphic Arts/Department of Graphic Design.*

- *Address: Technological Educational Institute (TEI) of Athens, Ag. Spyridonos Str., 12243 Aigaleo, Athens, Greece.*
- *Tel.: +0030- 210- 5385421, e-mail: stheochari@teiath.gr*

Thank you for your attention!

48th Conference of the International Circle of Educational Institutes for Graphic Arts Technology and Management

29 May to 2 June 2016

IC Leipzig 2016

Acknowledgements

This research is funded by the Special Account for Research Grants of the TEI of Athens, in the framework of the Internal Programme for the Support of the TEI of Athens Researchers, for 2015.

Authors also acknowledge DRUCKFARBEN Hellas S.A. for financial support.

TEI ΑΘΗΝΑΣ

DF DRUCKFARBEN BEYOND INKS... SOLUTIONS