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Printing on Anodized Aluminium Surface

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Abstract

Anodizing of aluminium is widely applied when a controllable morphology and properties of the surface are required. Anodic oxide films may be developed by appropriate selection of electrolyte and film-forming conditions for various applications in the fields of architecture, aerospace, electronics, packaging and printing. In the present study, the printability of aluminium with respect to anodizing conditions is discussed. In particular, AA1050 alloy specimens were anodized in either sulfuric acid or phosphoric acid at temperatures ranging from 10˚C to 40˚C, thereby affecting the porosity and anodic layer thickness. Both the porosity and oxide thickness increase with the temperature, whereas anodization in phosphoric acid produces thinner and more porous layer than that in sulfuric acid. After the anodization step, two different printing techniques were used (*i.e.* digital printing and screen printing). Printed specimens were characterized by means of colour parameters, microscopy, adhesion and light fastness test. Colour parameters and ink adhesion measurements indicate that both digital and screen printing techniques give a better print quality when the anodization step is conducted in the range of 20˚C - 30˚C.

Keywords

Aluminium, Aluminium Alloy, Surface Treatment, Anodizing, Anodic Oxide Film, Printing

1. Introduction

Among the various types of printing substrates for special or external applications (panels, signage, barcodes, awards, labels, etc.), aluminium has gain a great interest due to its superior decorative and fashionable design appearance; it is also a light weighting, long-lasting, recyclable material that ensures contemporary aesthetic, durability, light

fastness and resistance against chemicals.

Several processes are applied to modify aluminium surface properties and render it printable. The most effective one is the electrochemical treatment of anodizing. Anodizing of aluminium surface has received significant attention due to its diverse applications in various fields such as architecture, aerospace, electronics and packaging, but only a few special references are known in the field of printing and graphic arts. Such applications include lithography and various other special printing works [1]-[3].

The above mentioned uses of aluminium have enabled significant focus on fundamental aspects of anodic oxide film formation under controllable conditions in suitable electrolytes [4]. Among the various types of electrolytes used for anodizing, sulphuric (S.A.) and phosphoric acid (P.A.) solutions form porous anodic films on the aluminium surface. By anodizing, several types of oxide layers can be obtained depending on their effectiveness towards the electrolyte, and on the solvent power of the electrolyte of alumina [1]. Thus if the electrolyte is aggressive, such as sulphuric acid and phosphoric acid, the coating obtained consists of two parts: a thin non-porous compact layer at the metallic surface, which is known as the barrier layer, and an outer porous layer which is in contact with the electrolyte. The porous layer is usually about 10^3 - 10^4 times thicker than the barrier layer and it is composed of hexagonal cells in a honeycomb arrangement with a central pore perpendicular to the metal substrate [1]. When common aluminium alloys are anodized in sulphuric acid solution, a porous anodic coating is produced, the properties of which depend on the applied anodizing conditions [1]-[4]. Anodizing in phosphoric acid is rarely used in order to produce decorative or protective finishes, but it is being increasingly used as a preparative treatment for subsequent application of organic coatings, for adhesive bonding in the aerospace industry and for electroplating, due to the unique morphology of the oxide formed on the metal surface that interlocks with these coatings [1].

Many studies have been published on the modification of the porous structure as the anodizing conditions (*i.e.* voltage, time, temperature, electrolyte etc.) are altered [5]-[14]. The process of anodic oxide formation as well as the structure of the oxide is influenced by variation of the electrolyte temperature [11] [12]. It has been noted [11] that the aggressiveness of the electrolyte towards the oxide increases by increasing the electrolyte temperature, enhancing the chemical dissolution of the anodic oxide film by the electrolyte, thus resulting in a more porous and softer film. Under potentiostatic conditions, the increased aggressiveness of the electrolyte leads to higher steady state current densities, which imply a higher oxide formation rate. Equal anodizing time and applied potential will induce the formation of thicker oxide layers as the electrolyte temperature is increased, given that the maximum film thickness under the considered conditions is not reached. Additionally, the increase of the pore diameter towards the oxide surface becomes more pronounced by increasing the electrolyte temperature, due to the thermal enhancement of the chemical dissolution of the oxide by the electrolyte. As a result, the porosity of the oxide at the surface has been found to increase from 4% at 5˚C up to 32% at 55˚C [11].

The present work concerns aluminium as special printing substrate for specific applications under demanding conditions. Chemically pretreated AA1050 aluminium specimens were anodized in sulphuric or phosphoric acid solutions at various anodizing temperatures. Printing on anodized specimens by screen printing (using epoxy-catalytic inks) or inkjet printing (using UV curing inks) was followed by sealing in boiling water. Subsequently the $CIE_{L^*a^*b^*}$ and D_{CMYK} colour parameters of the imprint were evaluated and the optical and SEM micrographs were inspected. The relation of the characteristics (thickness and morphology) of the oxide layers formed under specific anodizing conditions with the printing quality of the anodized specimens, as well as the light fastness and adhesion of the imprint was investigated. The expected outcomes of the process described in the present paper are imprints of high quality and outdoor resistance and durability, on aluminum surface. Thus, a light weighting and recyclable material such as aluminum may be used more extensively.

2. Experimental

2.1. Pretreatment and Anodizing

Specimens of AA1050 aluminium alloy were degreased in acetone, etched for 1 min in a water solution containing 40 g/LNaOH at 40˚C rinsed with deionized water and immersed in 1:1 v/v concentrated HNO_3 at room temperature for 1 min. After rinsing with 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 of 15 V in 1.8 M H_2SO_4 (S.A.) for 40 min or at 30 V in 0.4 M H_3PO_4 (P.A.) for 5 min at various temperatures in the range 10˚C - 40˚C. Current transients during anodizing were recorded via a multimeter (Keithley 2000) connected with a PC.

2.2. Printing

Anodized specimens were printed by a laboratorial hand operated screen printing machine or by an Oce Arizona 350 XT digital printing machine. Printing was performed using epoxy-catalytic inks or UV curing inks accordingly and then sealed in boiling deionized water.

2.3. Characterization

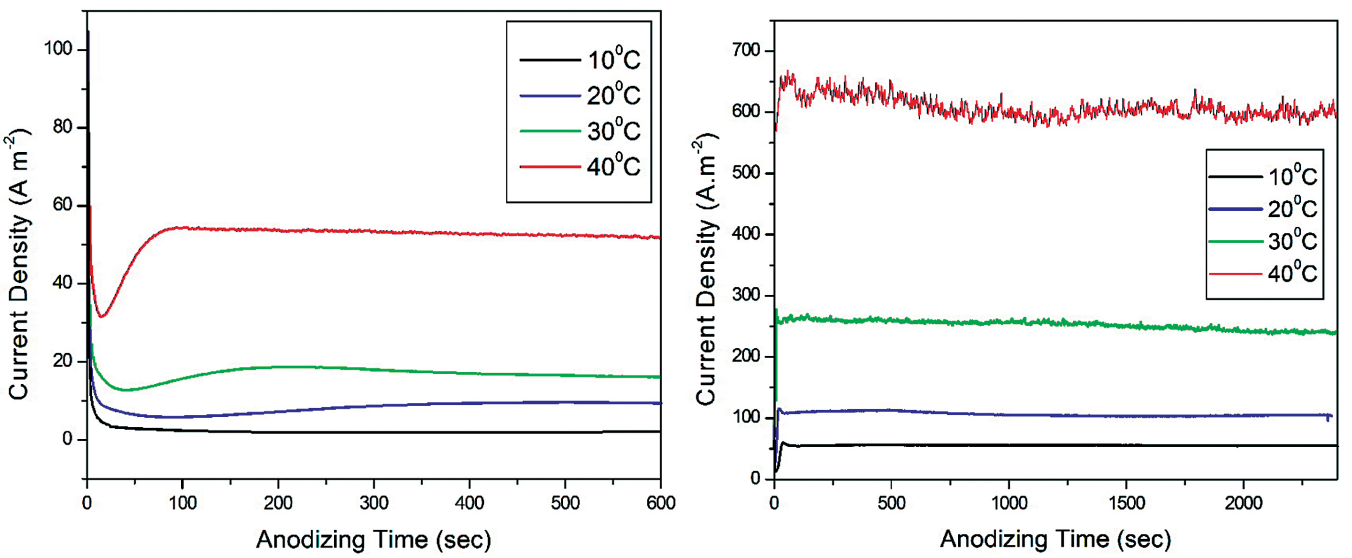
- A Spectro Eye (Gretag Macbeth) spectrophotometer was used for colour and print density measurements. Reflectance of printed specimens was measured with an Ocean Optics spectrophotometer (HR-2000modelequippedwith an optical fiber, Integrating Sphere, 50 mm, with glass trap, ISP-50-8-R-GT Micropack). Measurements were carried out via calibration with a standard Spectralon reflectance probe).
- Printed specimens were tested against common chemical solvents (water, acetone, ethanol) and evaluated according to ASTM D3359 (Measuring Adhesion by tape test) and ASTM D3424 (Light fastness evaluating). An optical stereo-microscope Olympus 5261 10 X - 80 X connected with a Sony Ex Wave HAD camera and PVR Plus software was used for surface images of the printed specimens.

- A JEOL JSM-6510 LV Scanning Electron Microscope (Oxford Instruments, 10mm^2 Silicon Drift Detector-x-act) was used for observation of the treated specimens.
- Image analysis was performed by using the Image J 1.50 b software in order to obtain quantitative information on the results of adhesion test on the printed surface of the specimens. The micrographs were 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.

The experimental procedure described above was performed for at least three times using distinctive specimens for each set of the selected experimental conditions. The obtained mean values of the measurements were used in order to ensure the reproducibility of the experiments.

3. Results and Discussion

The current density *vs.* time curves obtained during anodizing of AA1050 specimens in P.A. or S.A. at various temperatures are shown in Figure1. They show that a significant increase of current density occurs with increasing anodizing temperature. The values of the current density are about ten times higher in the case of S.A. compared to those of P.A. indicating that the consumed electric charge is much higher in the former case. Nevertheless, this charge results in an increase of the porous oxide layer thickness during the anodization process in both cases, while chemical dissolution of the oxide takes place leading to pore formation with an increased pore diameter towards the surface of the anodic alumina film, and accordingly to an increase of the film porosity especially at elevated temperatures [1] [11] [12].

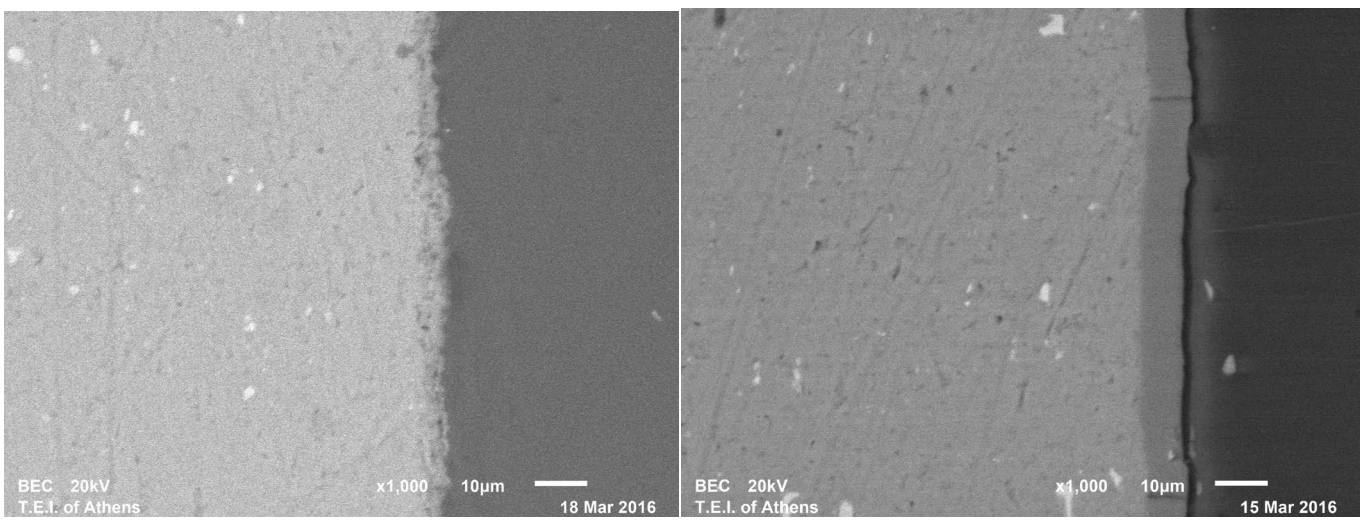


(a) (b)

Figure 1. Current density vs. time responses during anodizing at various temperatures of AA1050 specimens in 0.4M H_3PO_4 (P.A.) at 30 V for 5 min (a) and in 1.8 M H_2SO_4 (S.A.) at 15V for 40 min (b).

The anodic oxide films formed on AA1050 specimens in P.A. and S.A. at 20˚C are shown (cross-sectional view) as SEM micrographs in **Figure 2(a)** and **Figure 2(b)**, respectively, where the differences in the thickness and morphology of these films are evident. As can be seen the anodic oxide film formed in S.A. is thicker and well-defined compared to the one formed in P.A. which is thinner and very porous, with formations resembling protrusions or whiskers on its surface, in accordance to Wernick *et al.* [1].

Since differences in the structure and porosity or roughness of the surface of anodic oxide films influence their optical properties [15] [16], the reflectance spectra obtained from specimens that have been anodized in P.A. at various anodizing temperatures and printed by digital (inkjet) printing were recorded. The results are presented in **Figure 3**.



(a) (b)

Figure 2. Cross-section SEM images of oxide films on AA1050 specimens formed by anodizing in 0.4 M H_3PO_4 (P.A.) at 30 V for 5 min (a) and in 1.8 M H_2SO_4 (S.A.) at 15 V for 40 min (b) at 20˚C.

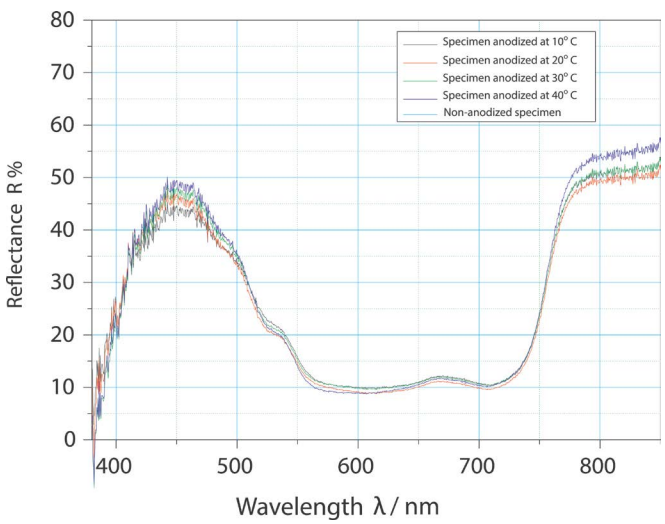


Figure 3. Reflectance spectra (R%) of digital printed specimens of anodized aluminium at various temperatures in 0.4 M H_3PO_4 (P.A.) at 30 V for 5 min, in the range of 380 - 850 nm.

In this figure, the observed λ_{max} values in all cases are observed in the region of 450 nm, which lies in the blue region and this is consistent with the experimentally used blue printing ink. It is also observed that while all these curves show similar shapes, they also show slight differences in the absolute values of R %, which indicate certain differences in the structure and porosity or roughness of the surface of the films formed at various anodizing temperatures.

The influence of the different acidic solutions (P.A. and S.A.) on the printability of anodized aluminium specimens was evaluated by the colour parameters $CIE_{L^*a^*b^*}$ and print density (D_{CMYK}). Anodizing was carried out in both acidic solutions at various temperatures ranging from 10˚C to 40˚C. The specimens were subsequently printed with UV curing ink by digital print and the results are shown in Figure 4 as optical microscopy images (X 50 and X 200) of printed specimens.

As can be seen in Figure 4 the anodized specimens in almost all the cases showed a very good printability compared to a non-anodized specimen. In the latter non-

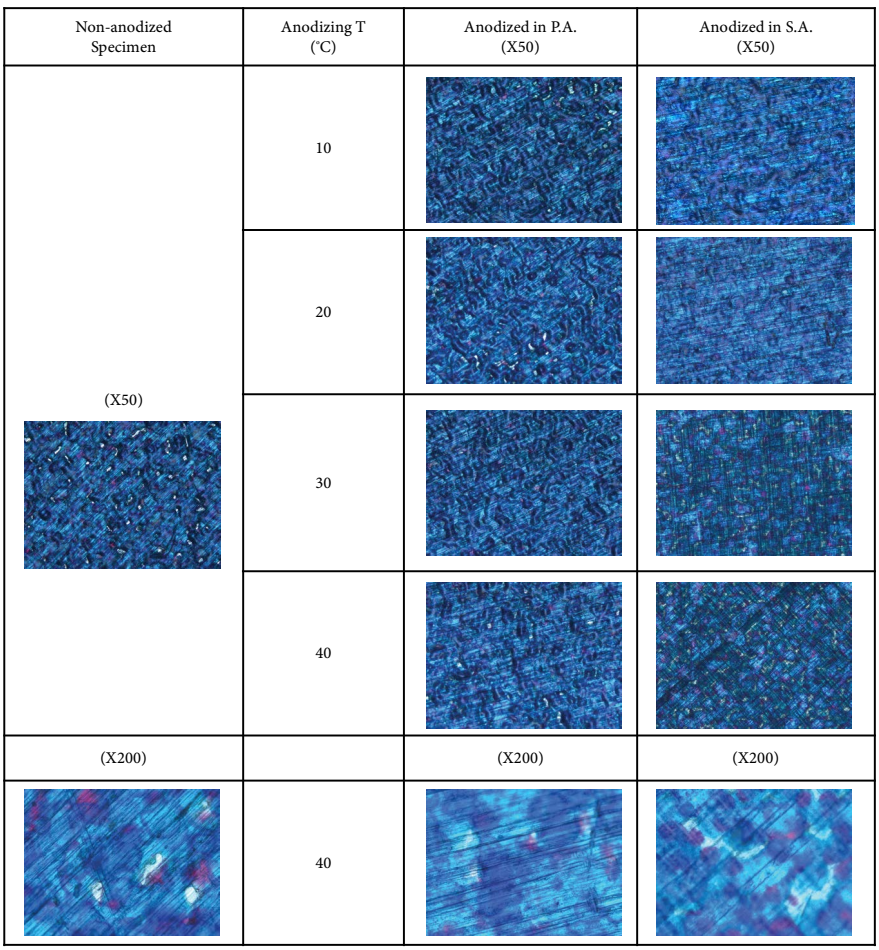


Figure 4. Optical photographs of the surface morphology of aluminium specimens, which were anodized in 0.4 M H_3PO_4 (P.A.) at 30 V for 5 min or in 1.8 M H_2SO_4 (S.A.) at 15 V for 40 min at various temperatures and printed by the digital printing method.

uniformities of the ink layer and some uncovered areas are evident. The optical observations are in accordance with the results regarding the colour parameters, which indicate that anodized specimens show very good printability. Thus, in the case of specimens anodized in P.A. at a temperature range of 10˚C - 30˚C, these parameters showed a rather unaltered printability with values in the range of 2.21-2.26 (D_C), 2.42-2.46 (D_M), 1.94 - 2.01 (D_Y), and 1.31 - 1.35 (D_K). These results are attributed to the fact that the anodic oxides formed in both P.A. and S.A. are of a highly porous and absorptive character, which permits the absorption of the ink and the formation of a uniform ink layer, as is confirmed from the images in **Figure 4**. However, the printed specimens that have been anodized at 40˚C (see **Figure 4**) show discontinuities and uncovered areas similar to those of the non-anodized specimens and indicate that anodizing at elevated temperatures favours dissolution of the film and possible phenomena of spongy and powdery oxide film modification [1] that in turn affects surface morphology and thus the quality of the imprint.

The results of the adhesion tape tests of the digital printed specimens anodized at different temperatures in P.A. and S.A. are presented in **Table 1**. It can be deduced that the morphology of the anodic films causes a gradual improvement of printing quality, with anodizing temperature (especially at 30˚C and 40˚C). These findings confirm the above mentioned modification of the structure of the anodic films, since elevated anodizing temperatures cause increased current density and subsequently larger amount of electric charge during the anodization process, while coating porosity is enhanced, due to the thermal field assisted dissolution and to the dissolution of the outer surface of the oxide layer [11]. The wide and open pores that are formed facilitate UV curing ink to be linked with the substrate. Thus, regarding the previous images (**Figure 4**) and the data of **Table 1**, it is concluded that in the case of digital printing with UV inks the best results are obtained from specimens anodizing in both S.A. and P.A. at temperatures ranging from 20˚C to 30˚C, with the latter considered to be the optimum one. Thus the choice of the appropriate temperature combined with the applied conditions of anodization appears to be a crucial advantage, since it improves the surface properties prior to printing.

The above findings are in good agreement with the values of the colour parameters

Table 1. Printed area removed (R.A. %) from digital printed specimens anodized at different temperatures in P.A. and S.A. after adhesion tape test (D3359 ASTM classification is given in parenthesis).

Anodizing T (˚C)	P.A. anodization R.A. %	S.A. anodization R.A. %
Non-anodized	89.0 (0 B)	89.0 (0 B)
10	60.0 (1 B)	90.1 (0 B)
20	14.9 (3 B)	91.1 (0 B)
30	2.7 (4 B)	2.3 (4 B)
40	0.2 (4 B)	0.0 (5 B)

D_{CMYK}, and especially of the Dc parameter, which is representative of the colour of the blue ink used in the case of specimens anodized at various temperatures in S.A. and printed by the digital-inkjet method, which are presented in Figure 5. As it is obvious from this figure this parameter obtains the highest value (Dc = 2.8) when anodization was performed at a temperature of 30˚C.

Considering the specimens anodized in P.A. and printed by screen print (the results are presented in Figure 6), local ink aggregates were observed on the printed surface at all temperatures of anodizing. A density of about 2.5 - 3.8 spots/mm^2 was observed except of the specimen anodised at 30˚C, for which the corresponding density value was 1.4 spots/mm^2. The average diameter of spots in all cases was 0.12 mm. The percentage

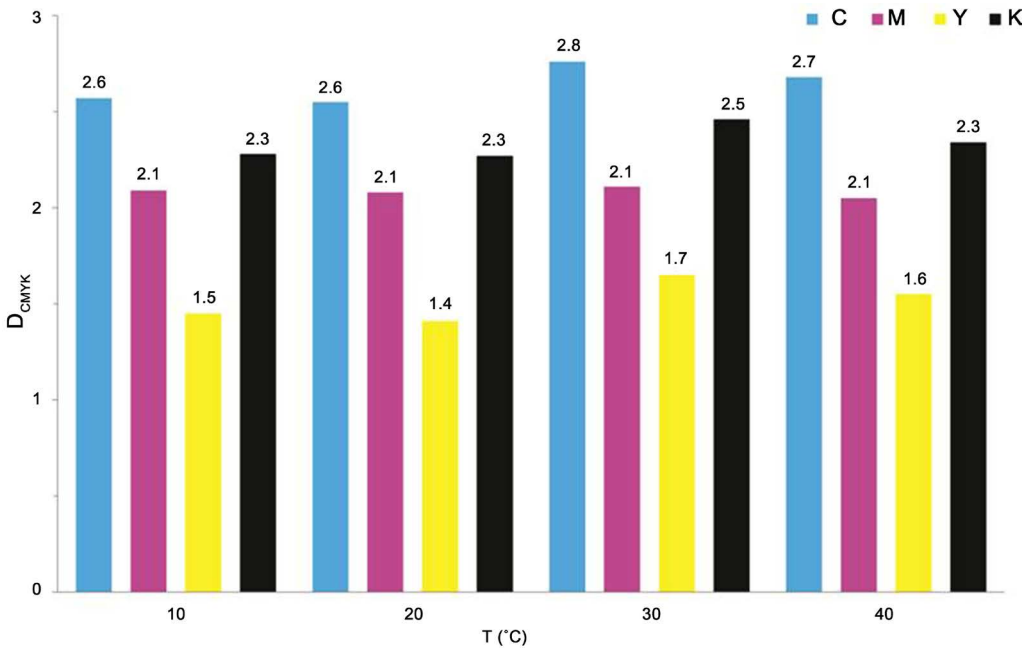


Figure 5. Colour parameters D_{CMYK} of aluminium specimens anodized at various temperatures in 1.8 M H_2SO_4 (S.A.) at 15 V for 40 min and printed by the digital inkjet method.

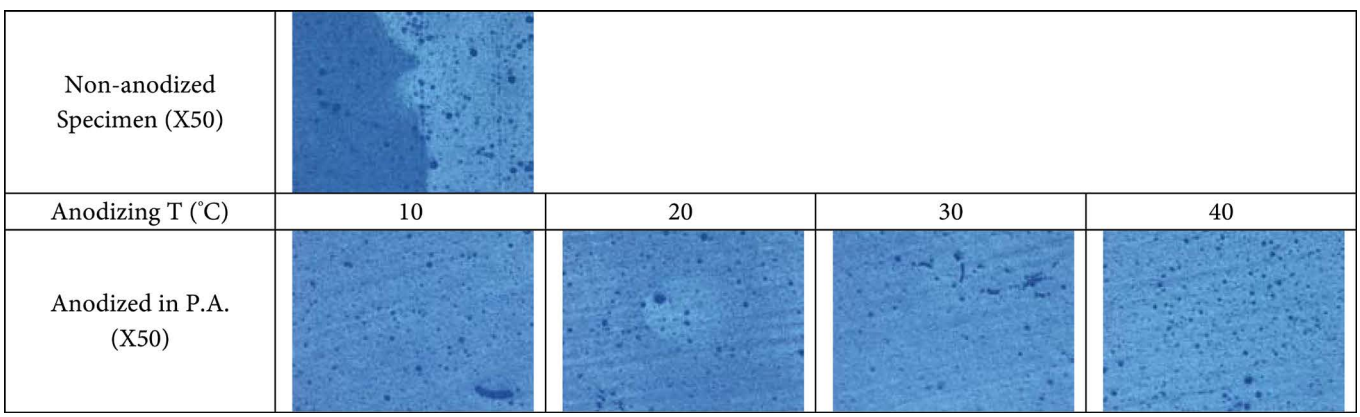


Figure 6. Optical photographs of surface morphology of aluminium specimens, which were anodized in 0.4M H_3PO_4 (P.A.) at 30 V for 5 min at various temperatures and printed by the screen print method.

area covered by such aggregates was 2.3% for the specimen anodised at 30˚C, while for the other temperatures was in the range of 2.6% - 3.6%. However, specimens anodised for 3 min rather than 5 min showed lower values of density with the optimum value of 0.4 spots/mm^2 in the case of anodized specimen at 30˚C while the average diameter of spots in all cases remained unchanged. The above results are in agreement with theories predicting that the anodic oxide films formed in phosphoric acid are very thin (about 3 μm), have large diameter pores [13] [14] and their morphology enables an adhesive or paint interlock [1].

From the above mentioned findings it is concluded that better imprints can be obtained in the case of screen print at anodizing temperatures slightly above room temperature applied for short anodization times. On the other hand, they are in good agreement with results of the adhesion tape tests on specimens anodized in P.A., which are presented in **Table 2**. From this table it is evident that in every case the anodic films showed excellent adhesion when the epoxy-based inks were applied by the screen print method. However, the aluminium specimens anodized in P.A. at 40˚C appear to be slightly affected (1% removed area) in accordance with the optical microscopy results mentioned above, suggesting that this particular temperature is a possible "threshold" value for the electrochemical treatment. The results obtained with the screen print method confirm the range of 20˚C -30˚C to be an advantageous one for the anodization under the conditions used, so that the quality of the imprint is improved. However, a further increase of the temperature above this range has a negative effect on print quality.

The above findings are in good agreement with the ones shown in **Figure 7**, in which the colour parameters CIE$_{L^*a^*b^*}$ of aluminium specimens, anodized at various temperatures in P.A. and printed by the screen print method, are presented. It is confirmed that the slightly highest value ($-b^* = 30.8$), which is representative of the colour of the blue ink that was used for printing tests in this study, is obtained for the specimen anodized at about 30˚C.

Finally, in order to investigate further the influence of the anodizing temperature on the printability of the anodized substrate, specimens anodized in S.A. solution at 20˚C and 25˚C were selected, since previous results had shown them to be the most promising. In this case epoxy-catalytic inks were applied on the anodized specimens by the

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

Anodizing T (˚C)	R.A. %
(Non-anodized)	0.4 (4B)
10	0.3 (4B)
20	0.3 (4B)
30	0.2 (4B)
40	1.0 (4B)

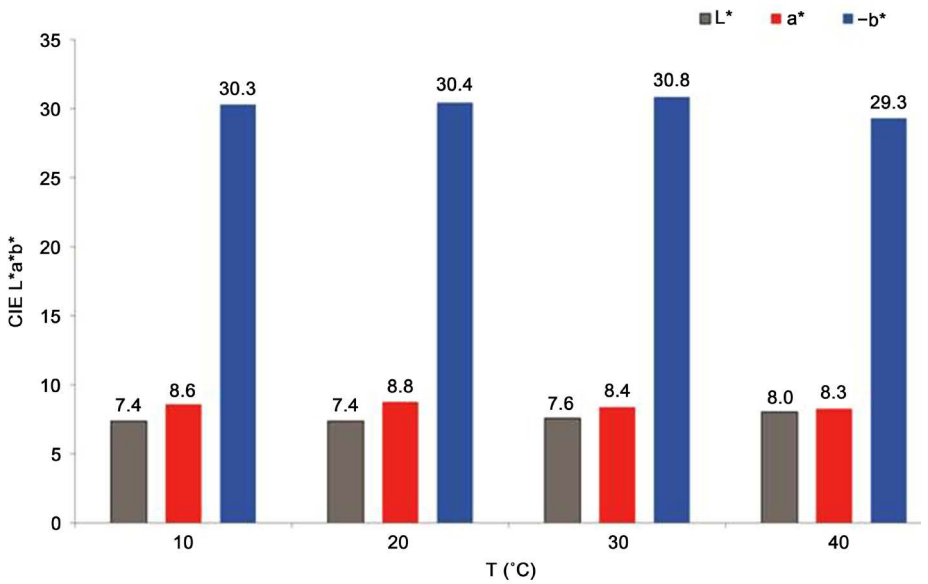


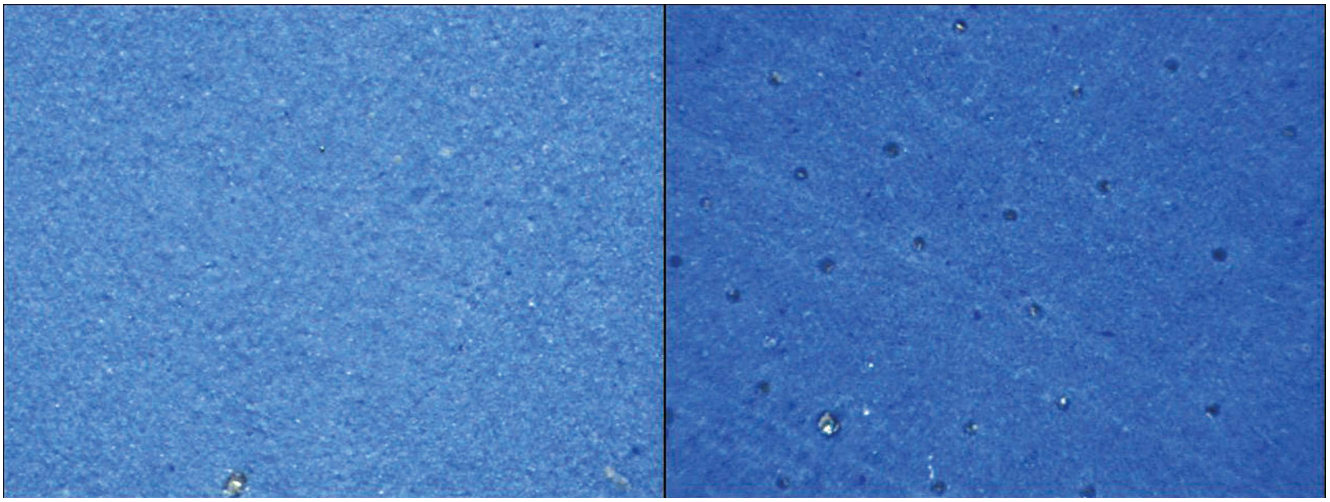
Figure 7. Colour parameters $CIE_{L^*a^*b^*}$ of aluminium specimens, which were anodized at various temperatures in 0.4 M H_3PO_4 (P.A.) at 30 V for 5 min, and printed by the screen print method.

screen printing method. Colour parameters $CIE_{L^*a^*b^*}$ determined by spectrophotometry, SEM cross-sectional microphotographs, as well as surface images (X30) of the printed specimens were recorded in order to evaluate the ink layer film on anodized aluminium specimens in the above mentioned conditions and the results are presented in **Figure 8**. They indicate a slight improvement of print quality $CIE_{L^*a^*b^*}$ ($\Delta E = 4.3$) with anodizing temperature (**Figure 8(e)** and **Figure 8(f)**), confirming that the film formed on aluminium substrate at a slightly elevated temperature has obtained suitable morphology and porosity that facilitates a better film forming by the ink. These findings are confirmed by SEM cross-sectional micrographs (**Figure 8(c)** and **Figure 8(d)**) which show a slightly thicker ink layer (23.6 μm) on aluminium specimen anodized at 25˚C compared to the ink layer thickness (20.7 μm) on the one anodized at 20˚C. However, the optical photographs of the printed surface of specimen anodized at 25˚C showed also the initiation of certain defects and imperfections on the surface of the specimen having the form of pits (**Figure 8(a)** and **Figure 8(b)**). This fact indicates that increasing anodizing temperature improves the printability of the surface but it also leads to the initiation of its deterioration.

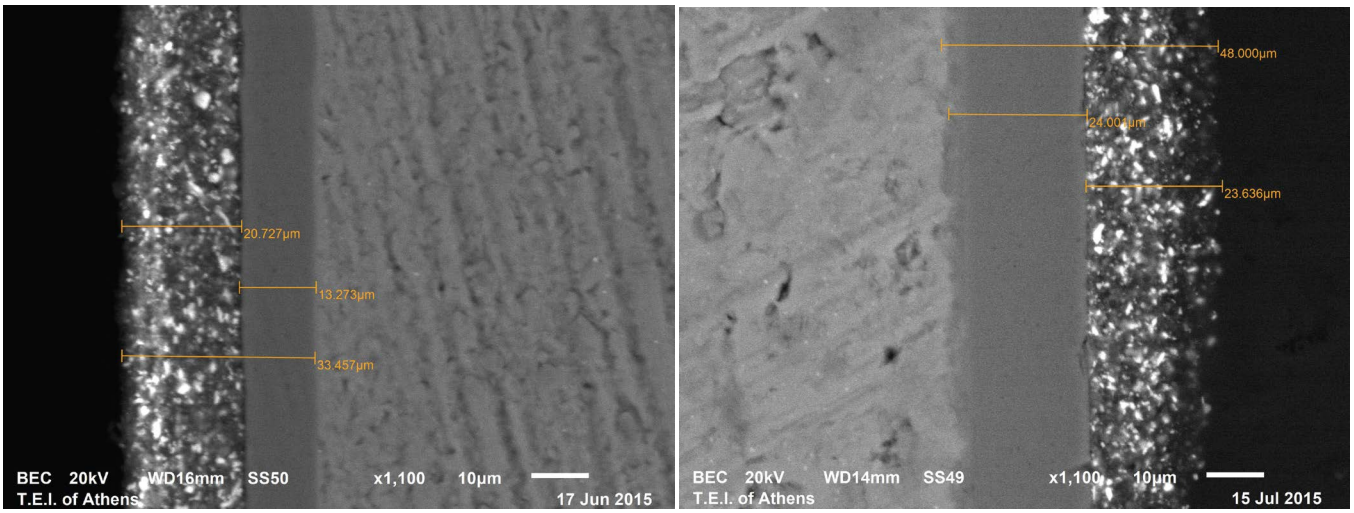
It should be mentioned that all specimens anodized and printed with the epoxy-based inks applied by screen print method gave excellent adhesion tape test results (R.A. % values of 0.0 - 0.5). They also showed excellent light fastness and fastness against common chemical solvents (water, ethanol, acetone) indicating that the suggested method may be used as an excellent pretreatment process for aluminium surface prior to printing by either digital printing or screen print methods.

4. Conclusions

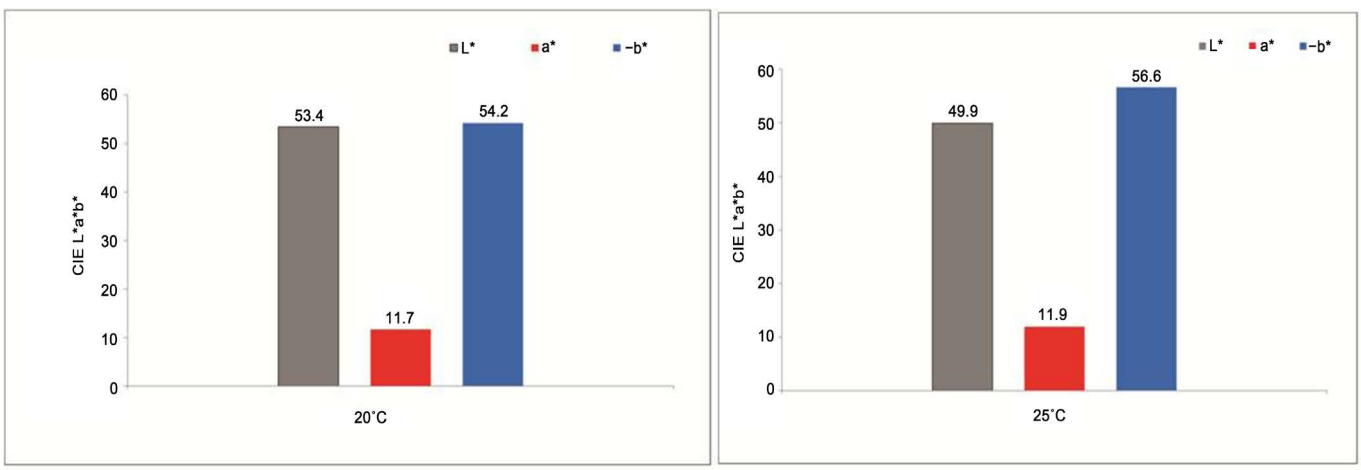
Commercially pure aluminum (AA1050) specimens were anodized and printed with



(a) (b)



(c) (d)



(e) (f)

Figure 8. Optical photographs (X30), SEM cross-sectional views of anodized aluminium printed specimens anodized in S.A. (1.8 M H_2SO_4, 15 V, 40 min) together with the corresponding $CIE_{L^*a^*b^*}$ parameters of the printed specimens at 20˚C (a, c, e) and 25˚C (b, d, f).

UV curing ink by digital and with epoxy-based inks by screen printing methods. As expected, it was observed that surface properties of anodic oxide films depended on the type of anodizing electrolyte and on anodizing temperature. A suitable modification of the surface of aluminum substrate results in an improvement of the quality and the outdoor resistance of the imprint. Specifically, the weatherability and resistance against chemicals as well as the protection from sunlight were improved.

In the case of P.A. anodization (thin anodic oxide films for internal applications), an increase of the anodizing temperature results in an improvement of print quality (colour parameters and adhesion test) of printed specimens by both methods and materials; in the case of epoxy-based inks applied by screen print method, the best results were obtained in the range of 20˚C - 30˚C. Printed specimens anodized at 30˚C gave also excellent results on print density and adhesion resistance especially in the case of the UV curing inks.

In the case of S.A. anodization (thick anodic films and protective against external effects), a slight increase of the electrolyte concentration or the anodizing temperature results in an improvement of print quality of specimens (colour parameters, adhesion and light fastness test, resistance against chemicals), especially when epoxy-based inks are applied by the screen print method. In the case of the UV curing ink printed specimens anodized at 30˚C gave also excellent results concerning the print density and the adhesion resistance.

Pretreatment of aluminium substrates under the conditions described in the present paper is expected to advance the use of the studied procedure, in order to improve the quality of the imprints, especially for outdoor and other demanding applications. The scientific outcomes may thus be combined with practical applications in the field of printing technology. As anodizing turns out to be an excellent treatment of aluminium surface prior to printing, especially in the case of specific applications (barcodes, labelling, panels, etc.) or when excellent adhesion, resistance properties and quality of printed specimens are required, clarification of the anodizing conditions would be of interest for further investigation. The influence of anodizing parameters combined with the various types of inks and printing techniques on print quality would be of great academic and commercial interest.

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