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RESEARCH PAPER

THE EFFECT OF DIFFERENT PRE-SURFACE FINISHING METHOD ON THE ALUMINIUM ANODIZATION OF THE 6XXX SERIES ALLOY

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ABSTRACT

In this study, the effect of different pre-surface finishing methods on the aluminium anodization was investigated for AA 6063 alloy. Within the scope of pre-surface finishing method which is an acidic solution, the effects of concentrations and process time were determined. Acidic solution was determined by using hydrofluoric acid (HF) and nitric acid (HNO_3). Also Gresoff LIM-5 LV chemical was used with different concentrations and process time for degreasing process. The etching effect of acidic solution on aluminium samples was investigated. The optimal etching behaviour was obtained with 1.0% concentration of HF and 3.2% concentration of HNO_3 at 10 minutes process time. Also optimal surface properties were observed with 1.0% concentration of Gresoff LIM-5 LV at 12 minutes process time. Then anodic oxidation was performed by using 180 g/L sulfuric acid (H_2SO_4) and 18 volt (V). Surface morphology of the final aluminium profiles were examined with SEM analysis, Roughness, Gloss and Thickness tests.

Keywords: Aluminium; 6XXX alloy; Anodic Oxidation; Pre-Surface Finishing, Corrosion

INTRODUCTION

Aluminium is a relatively light metal with a specific density of 2.7 g/cm^3 compared to metals such as steel, nickel, brass, and copper. Also aluminium and its alloys can be easily machined and exhibits a wide variety of surface properties. It also has good electrical and thermal conductivities [1]. Aluminium alloys have a wide range of applications for various purposes in many different industries due to their properties such as low density, high strength, superior mechanical behavior and workability [2].Al-Mg-Si system has a high fabricability. 6XXX aluminium alloy series which is defined Al-Mg-Si system is one of the widely used in application area [3]. Many research show that inadequate corrosion and mechanical properties and also surface quality have restricted their application usage [4]. It's known that the anodic oxidation forming of the aluminium alloys which has a highest mechanical properties negatively affect fatigue performance [5]. Anodic oxidation is called electrochemical composition is widely used method for improving surface performance and also quality in application area [6]. Anodic oxidation process is defined to occur the homogeneous oxide layer. Pre-surface finishing is used to remove the uncontrolled oxide layer of the aluminium surface [7]. This uncontrolled oxide layer typically has a less than 1-2µm. The oxide film is obtained by anodizing process has 20-50µm and also durable to other corrosion attacks [8]. Many reviews on the structure of the anodically formed aluminium oxide film, content of the anion, the amount of water bound depending on the structure of the surface oxide had been performed [9]. Aluminium is an active metal that will behave anodically against all elements except the alkali and alkaline earth metals. Aluminium and its alloys can oxidize very rapidly under atmospheric conditions on the surface. The method of forming the protective oxide film on the metal surface in order to prevent or slow down corrosion is called anodization (anodic oxidation). Anodic oxidation which is one of the aluminium coating methods is a process based on the formation of a controlled oxide layer by an electrochemical method [10]. The method of forming a protective oxide film or layer on the metal in order to prevent or slow down corrosion is called anodization which is defined pre-surface finishing process. In other words, anodic oxidation can be defined as an electrochemical process in which a controlled oxide layer is formed on the metal surface [11]. Pre-surface finishing processes directly affect the adhesion, optical/mechanical properties and homogeneity of the anodized coating on the surface [12]. A review on the structure of the anodically formed aluminium oxide film, the anion content, the amount of water bound depending on the structure of the oxide, and the properties caused by these structural differences was first published in 1968 [13].There are many parameters which affect the anodized coating properties (homogeneity, adhesion) of the aluminium extrusion profiles. These parameters can be categorized by the presence of intermetallic phases, grain size and structure, etching capability of the pre-surface finishing solution [14]. Pre-surface finishing method directly affects the anodic oxidized coating's quality. The pre-surface finishing method is extremely critical to create a strongly adhered anodized coating on extruded aluminium surfaces [15]. Some problems with the aluminium surface can be observed such as adhesion, strength, homogenous thickness, when the chosen pre-surface finishing method is not suitable for the given aluminium alloy [16]. The pre-surface finishing process enable to controlled abrasion of the aluminium surface to ensure adhesion. This process is called etching+matting process gives a more effective result in acidic baths than in alkaline baths. The mechanism in alkaline baths is based on the esterification reaction. Alkaline baths remain more passive as they saponify the oil residues formed during extrusion by esterification reaction [17] The acidic baths acts more effective on oil residue and dirt in the micropore of aluminium profile [18]. It has been reported that the pre-treatment is not only must provide the structural bonding of aluminium alloy but also must provide strong mechanical properties and corrosion resistance [19]. It has been studied about corrosion behavior of AA6063 in acidic and in alkaline media. The corrosion rate of 6063 aluminium alloy has a higher degree in sodium hydroxide than in phosphoric acid was found. It was found that the corrosion rate of 6063AA increased in the acidic concentration as well as in the alkali concentration [20]. In this study, it's aimed to development of an acidic pre-treatment bath, which is more effective instead of the alkaline pre-treatment bath. It can be achieved that the homogeneous etching surface along the aluminium profile surface, and also coating surface. Thus, it will be obtained that the controllable and repeatable process.

MATERIAL AND METHODS

Etching Process

The anodic oxidation process on the aluminium material surfaces having been shaped by extrusion is performed in acidic baths under high voltage with controlling the current density. In this way the aluminium surface must gain higher roughness by this etching process before anodic oxidation process. Also the removal of the natural oxide film from aluminium surface plays a critical role to the quality of the so formed controlled oxide film [14]. Generally conventional alkaline solution with an application temperature of around 60 °C which removed oil residues on the surface by esterification reaction may be insufficient at this stage. The acidic solution was improved for etching process in this study. Hydrogen fluoride (HF) with 38 % - 40 % purity and nitric acid (HNO3) with 50 % purity were used in the etching process. Chemical composition of 6063 aluminium alloy profiles were used experiment studies is given **Table 1**. Also the concentration (%) of acidic solution is given in **Table 2**.

Table 1 Chemical Composition of AA6063

Fe	Si	Cu	Mn	Mg	Zn	Cr	Al	Other
				%				
0.22	0.42	0.008	0.0073	0.47	0.01	0	0.988	0.15

Table 2 Concentration (%) of acidic solution

	HNO_3 %	HF %	Time (min)	pH	Temperature (°C)
Sample 1	3.2	0.10	1	1.80	25
Sample 2	3.2	0.10	2	1.80	25
Sample 3	3.2	0.10	3	1.80	25
Sample 4	3.2	0.10	5	1.80	25
Sample 5	3.2	0.10	10	1.80	25
Sample 6	3.2	0.20	1	1.80	25
Sample 7	3.2	0.20	2	1.80	25
Sample 8	3.2	0.20	3	1.80	25
Sample 9	3.2	0.20	5	1.80	25
Sample 10	3.2	0.20	10	1.80	25
Sample 11	3.2	0.30	1	1.80	25
Sample 12	3.2	0.30	2	1.80	25
Sample 13	3.2	0.30	3	1.80	25
Sample 14	3.2	0.30	5	1.80	25
Sample 15	3.2	0.30	10	1.80	25
Sample 16	3.2	0.50	1	1.80	25
Sample 17	3.2	0.50	2	1.80	25
Sample 18	3.2	0.50	3	1.80	25
Sample 19	3.2	0.50	5	1.80	25
Sample 20	3.2	0.50	10	1.80	25
Sample 21	3.2	0.70	1	1.80	25
Sample 22	3.2	0.70	2	1.80	25
Sample 23	3.2	0.70	3	1.80	25
Sample 24	3.2	0.70	5	1.80	25
Sample 25	3.2	0.70	10	1.80	25
Sample 26	3.2	1.0	1	1.80	25
Sample 27	3.2	1.0	2	1.80	25
Sample 28	3.2	1.0	3	1.80	25
Sample 29	3.2	1.0	5	1.80	25
Sample 30	3.2	1.0	10	1.80	25

Degreasing Process

The composition content of degreasing process is given in **Table 3**.

Table 3 Concentration (%) of Gresoff LIM-5 LV

Alloy	HNO_3 %	HF %	Gresoff LIM-5 LV %	Time (min)	pH	Temperature (°C)
6063	3.2	1.0	1.0	1	1.90	25
	3.2	1.0	1.0	2	1.90	25
	3.2	1.0	1.0	3	1.90	25
	3.2	1.0	1.0	4	1.90	25
	3.2	1.0	1.0	5	1.90	25
	3.2	1.0	1.0	6	1.90	25
	3.2	1.0	1.0	7	1.90	25
	3.2	1.0	1.0	8	1.90	25
	3.2	1.0	1.0	9	1.90	25
	3.2	1.0	1.0	10	1.90	25
	3.2	1.0	1.0	11	1.90	25
	3.2	1.0	1.0	12	1.90	25

Anodic Oxidation Process

Anodic oxidation was performed with 180 g/L H_2SO_4 and 18 V. The anodic oxidation electrochemical reaction process is given in **Fig. 1**. Also equation 1 displays anode, cathode and net reaction in anodic oxidation process.

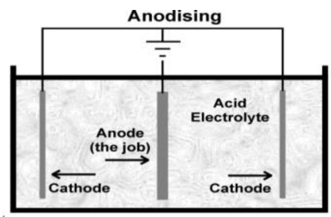


Fig. 1 The Anodizing Electrochemical Reaction

Anode Reaction: $2Al + 3H_2O = Al_2O_3 + 6H^+ + 6e$-

Cathode Reaction: $6H$+ $6e^- = 3H_2$

Net Reaction: $2Al + 3H_2O = Al_2O_3 + 3H_2$ (1.)

The aluminium is connected as anode to the positive end of the power supply in a suitable electrolyte bath (phosphoric acid, sulfuric acid, or chromic acid, etc.) in the anodic oxidation process. The cathode can be carbon rod or plate, nickel, lead, or stainless steel and is connected to the negative end of the power supply. Electrolysis process is carried out under direct current (DC). Metal ions on the aluminium metal surface formed on the anode react with oxygen to form metal oxide form. All oxide development processes are aimed at obtaining the outer porous oxide layer with the desired properties. The pore structure of this layer depends on the type of environment in which the oxidation process is performed, the application time of the potential, the temperature and the pH of the environment [15].

RESULTS AND DISCUSSION

Optical Microscope Test

Optical microscope images of the unprocessed profile are given in **Fig. 2**. It was observed that surface defects and oil residual are there on the profile when no pre-surface treatment is applied after extrusion. The Nikon Eclipse MA 100 was used by using Clemex Vision Lite program (Zahit Alüminyum Research and Development Center, Adana, Turkey).

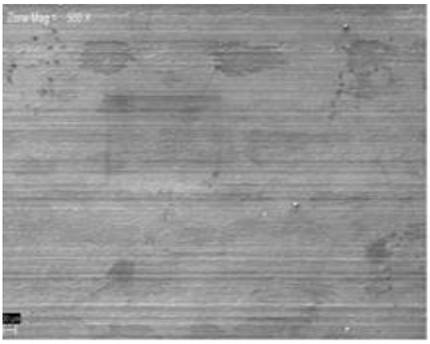


Fig. 2 The Unprocessed Aluminium Profile

Optical microscope images of the pre-surface treatment performed by using Polytoxal DG15 alkaline solution with 13 pH at 8 minutes process time is given in **Fig. 3**. It was observed that the aluminium which treated Polytoxal DG15 was carried out etching and removed impurities from the surface.

Fig. 3 Polytoxal DG15 Treated Profile

Optical microscope images of the pre-surface treatment performed by using 1.0 % concentration of HF and 3.2 % concentration of HNO_3 at room temperature at 10 minutes process time is given **Fig. 4**.

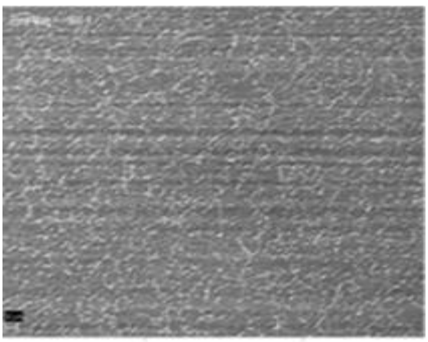


Fig. 4 Nitric acid (HNO_3) and Hydrogen fluoride (HF) Treated Profile

It was found that the aluminium profiles which was treated HF and HNO_3 was carried out etching and removed from the impurities on the surface. It appears to be a more suitable surface for anodizing. It can be concluded that this surface morphology directly will be positive affected anodic oxidation capability. Surface morphology exhibits more homogeneous abrasion behaviour in **Fig. 4**. Its mean that the accessing of micropore and surface cleanliness can be achieved more effectively by using solutions with certain percentage of HNO_3 and HF. Especially it was found that the abrasion behaviour. It appears to more stable surface properties such as etching capability, roughness homogeneity were compared to other pre-surface finishing method which was used alkaline solution (Polytoxal DG15).

Roughness Test

Roughness test results for all samples which belong to different pre-surface finishing methods are given in **Fig. 5**. Surftest SJ-210 test device (Çukurova University, Central Research Laboratory, Adana, Turkey) was used in the surface roughness test.

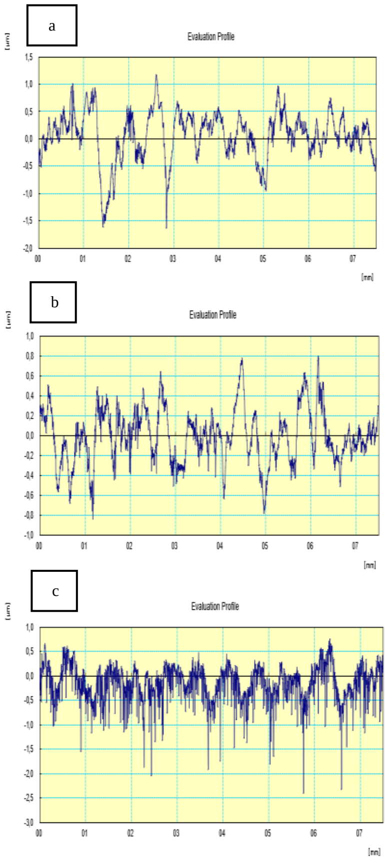


Fig. 5 Surface roughness measurements; a) Roughness test of aluminium profile unprocessed, b) Roughness test of aluminium profile treated Polytoxal DG15, c) Roughness test of aluminium profile treated hydrogen fluoride (HF) and nitric acid (HNO_3)

Roughness test of aluminium profile that was treated with 1.0 % concentration of HF and 3.2% concentration of HNO_3 at room temperature at 10 minutes process time displays more homogeneous etching. It can be concluded that more homogeneous etching behaviour of the surface will affect the anodizing ability positively. **Table 4** shows comparative analysis of different pre-surface finishing methods with Ra and Rz values. When the Ra represents the mean roughness value, the Rz represents roughness depth. Also RPc is peak count that corresponds to the number of local peaks.

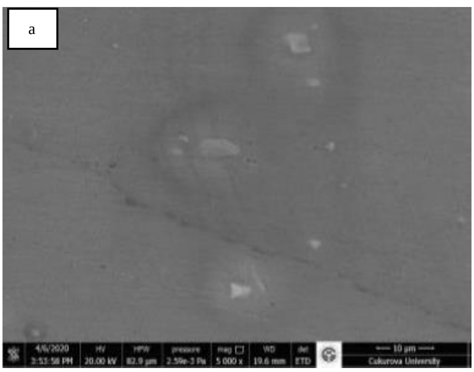
Table 4 Comparative analysis with different pre-surface treatment

	Ra (µm)	Rz (µm)	RPc (/cm)
Aluminium profile unproccesed	0.347	2.449	14.12
Aluminium profile treated Polytoxal DG15	0.215	1.469	17.21
Aluminium profile treated HF and HNO_3	0.303	2.752	46.22

The 10 different roughness measurements were performed at one side for all samples. The measurements direction is along of the extrude aluminium profile length that can be defined as a extrusion exit direction. The Ra (µm), Rz (µm) and Rpc (/cm) values represent the average values of different measurements at one side for all samples which is indicated in Table 4. It was observed that the etching of the aluminium profile treated with 1.0 % concentration of HF and 3.2 % concentration of HNO_3 at room temperature at 10 minutes process time exhibits more ideal behaviour. It can be deduced that the controlled etching process will be reached with HF and HNO_3 as seen Fig. 5. The pre-surface finishing method by using Polytoxal DG15 is standard process in serial production. The Ra (µm) roughness value is 0.215, the Rz (µm) roughness value is 1.469 for standard process as a given in Table 4.This values are respectively 0.303 and 2.752 for improved pre-surface finishing method by using HF and HNO_3. The Ra (µm) and Rz (µm**)** values of improved process are higher than the standard process. It's mean that the abrasion behaviour was obtained more efficiency than the standard process. Thus, the anodic oxidation coating can exhibit more homogeneous behaviour all along of aluminium profile surface. Also the anodic oxidation coating can most efficient hold on to aluminium profile surface.

SEM Analysis

SEM analysis was carried out for sample that was performed pre-treatment process by using 1.0 % concentration of HF and 3.2 % concentration of HNO_3 at room temperature at 10 minutes process time. SEM analysis results are given in **Fig. 6**. Tescan Vega test device (Çukurova University, Central Research Laboratory, Adana, Turkey) was used in SEM analysis.



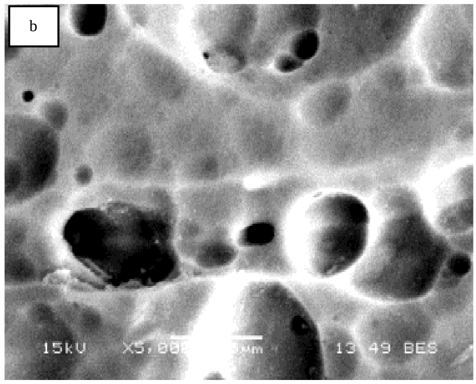


Fig. 6 SEM analysis of aluminium profile with coating; a) Aluminium profile with Polytoxal DG15,b) Aluminium profile with HF and HNO_3

The thickness of anodic oxidation coating is given **Fig. 7**. The optimal pre-surface finishing parameter which is concentration of 1.0% HF and 3.2% HNO_3 were used in anodic oxidation process. Also Gresoff LIM-5 LV was used concentration of 1.0%.

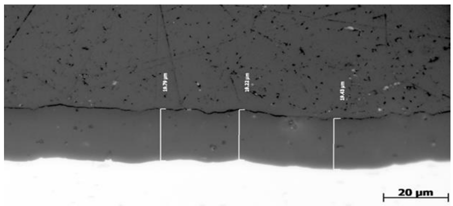


Fig. 7 SEM Image of HF and HNO_3 Treated Eloxal Coated Profile

Gloss and Thickness Test

The samples were used for measurement of the stability of improved pre-surface finishing method. Thickness and gloss measurements were performed. Measurements of coating thickness and gloss which belong to different pre-surface finishing method are given in **Table 5**.

Table 5 Thickness and Gloss measurement of different pre-surface treatment

	Aluminium profile with Polytoxal DG15		**Aluminium profile with HF and HNO_3 and Gresoff LIM-5 LV**	
	Thickness (µm)	**Gloss**	**Thickness (µm)**	**Gloss**
Sample 1	12.3	17	12.4	31.1
Sample 2	13	26.8	12.3	28.7
Sample 3	12.3	27.9	13.2	31.1
Sample 4	13.7	24.8	13.3	28.8
Sample 5	11.8	23.8	12.3	28.2
Sample 6	12.9	26.3	12.7	31.1
Sample 7	12.6	24.8	13.7	31
Sample 8	12.4	27.6	12.6	30.1
Sample 9	12.4	22.9	12.8	29.3
Sample 10	12.6	23.4	12.8	31.1
Standard Deviation	0.51	3.17	0.46	1.19

It was found that the pre-surface finishing method with 1.0% concentration of HF and 3.2 % concentration of HNO_3 exhibits more stable etching behaviour. And it can be deduced that this process ensures reproducibility quality standard, which reproducibility is very important in terms of atmospheric corrosion resistance and physical properties of final product.

CONCLUSION

It was aimed to apply a pre-surface finishing method that contains the etching and degreasing process combined in one acidic solution. Generally caustic soda solutions are used for the anodizing preparation of the aluminium surface. This process is called causticization generally is operated at about 60 °C.

- In this study, the experiments were performed with different concentrations that are between 0.1% and 1.0% of HF with 3.2 % concentration of HNO_3 at room temperature.
- Experimental studies were carried out with 38% - 40% purity Hydrogen Fluoride (HF), 55% purity Nitric Acid (HNO_3), Gresoff LIM-5 LV chemicals and with 18V.
- The etching capability was investigated at different concentrations and process time. Optimal etching capability parameters were observed which are concentration of 1.0 % HF and 3.2 % concentration of HNO_3 and 10 minutes process time was used for improving degreasing during the experiment studies.
- Degreasing studies were performed with 1.0% concentration of Gresoff LIM-5 LV chemicals and process time between 1 and 12 minutes.
- The optimal surface morphology was obtained with 12 minutes for degreasing process.
- Then anodic oxidation was applied on the aluminium profiles which were exposed to pre-surface finishing process.
- The roughness test, microstructure test, thickness and gloss measurement were also performed in this study.
- The standard deviation value of thickness and gloss measurement were calculated.
- It was observed that the standard deviation with improved acidic solution is smaller than with the alkaline solution.

It can be concluded that this improved pre-surface finishing method can be well adjusted to improve the etching capability and remove oil residual from the surface. The thickness measurement standard deviation of standard process is higher than the standard deviation of improved pre-surface finishing process. The stability of the coating thickness measurement values of aluminium profile treatment standard pre-surface finishing used Polytoxal DG15 was not obtained in serial production. Its mean that the measurements differ from each other was taken at different point of the same aluminium profile. This behaviour can negative affects anodic oxidation quality and homogeneity. Thus, the coating thickness wouldn't homogeneity along the aluminium profile surface. Also the analysis and tests show that the improved pre-surface finishing method by using concentration of 1.0 % HF and 3.2 % concentration of HNO_3 at 10 minutes process time provided more homogeneous abrasion. We found that the Rz (µm) value of aluminium profile was treatment by using improved pre-surface finishing method is highest. It's mean that the anodic oxidation coating deeply holds on the aluminium profile surface. Also standard deviation of coating thickness is lowest. Its mean that its not only the coating deeply hold on the aluminium profile surface, but also the abrasion exhibits same behaviour along the aluminium profile surface. This means that the surface quality was improved by obtaining a repeatable process. These standard deviation values are an important output in obtaining a repeatable and controllable front surface treatment process. Also its obtained that the controllable and repeatable process achieved with a decrease in the standard deviation value. The process that has proven to be statistically high in repeatability and thus obtaining a standard surface quality is one of the most important outputs.

REFERENCES

1. A. Mozalev, A. Poznyak, I. Mozaleva, A. W. Hassel: Electrochemistry Communications, 3(6), 2001, 299-305. https://doi.org/10.1016/S1388-2481(01)00157-6.
2. P. Bocchetta et al.: Journal of Applied Electrochemistry, 32(9), 2002, 977-985. https://doi.org/10.1023/A:1020960719245.
3. H. Habazaki., M.A. Paez, K. Shimizu, P. Skeldon, G.E. Thompson, G.C. Wood, X. Zhou: Corrosion Science, 38(7), 1996, 1033-1042. https://doi.org/10.1016/0010-938X(96)00184-9.
4. X. Nie, A. Leyland, H.W. Song, A.L. Yerokhin, S.J. Dowey, A. Matthews: Surface Coating Technology, 116-119, 1999, 1055-1060. https://doi.org/10.1016/S0257-8972(99)00089-4.
5. E. Cirik, K. Genel: Surface and Coating Technology, 202(21), 2008, 5190-5201. https://doi.org/10.1016/j.surfcoat.2008.06.049.
6. X. Li, X. Nie, L. Wang, D. Northwood: Surface and Coatings Technology, 200(5-6), 2005, 1994-2000. https://doi.org/10.1016/j.surfcoat.2005.08.019.
7. F. Andreatta, H. Terryn, J.H.W. de Wit: Electrochimica Acta, 49(17-18), 2004, 2851-2862. https://doi.org/10.1016/j.electacta.2004.01.046.
8. M. Ardelean, S. Lascau, E. Ardelean, A. Josan: Materials Science and Engineering, 294, 2018, 1-11. https://doi.org/10.1088/1757-899X/294/1/012042.
9. Q. Li, J. O. Jensen, N. J. Bjerrum: Encyclopedia of Electrochemical Power Sources, 2009, 695-708.
10. V. Moutarlier, M. P. Gigandet, J. Pagetti, L. Ricq: Surface and Coatings Technology, 173(1), 2003, 87-95. https://doi.org/10.1016/S0257-8972(03)00511-5.
11. Anon: The Properties of Aluminium and its Alloys. Aluminium Federation, Halesowen, 1968.
12. W. Lee: Springer Series in Materials Science, 219, 2015, 107-153, https://doi.org/10.1007/978-3-319-20334-8_4.I.
13. Tsangaraki-Kaplanoğlu, S. Theohari, Th. Dimogerontakis, Y-M. Wang, H-H. Kuo, S. Kia: Surface and Coatings Technology, 200(8), 2006, 2634-2641. https://doi.org/10.1016/j.surfcoat.2005.07.065.
14. M. Erbil: *Corrosion of aluminum in various aqueous solutions*, Ph.D Thesis, Institute of Science, Adana, 20-21, 1975.
15. Erbil, M., *Corrosion rate of aluminum in lactic acid solution*, MSc. Thesis, Institute of Science, Adana, 10-11, 1971.
16. V. Moutarlier, M. P. Gigandet, J. Pagetti, B: Normand Surface and Coatings Technology, 182(1), 2004, 117-123. https://doi.org/10.1016/S0257-8972(03)00875-2.
17. J. Ren, Y. Zuo: Surface and Coatings Technology, 182(2-3), 2004, 237-241. https://doi.org/10.1016/j.surfcoat.2003.08.082.
18. F. Mansfeld, H. Xiao, L.T. Han, C.C. Lee: Progress in Organic Coatings, 30(1-2), 1997, 89-100. https://doi.org/10.1016/S0300-9440(96)00675-3.
19. J-S. Zhang, X-H. Zhao, Y. Zuo, J-P. Xiong: Surface and Coating Technology, 202(14), 2008, 3149-3156. https://doi.org/10.1016/j.surfcoat.2007.10.041.
20. D. Prabhu, P. Rao: Arabian Journal of Chemistry, 10(2), 2017, S2234-S2244. https://doi.org/10.1016/j.arabjc.2013.07.059.