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Studies on Electrochemical Oxidation of Aluminum and Dyeing in Various Additives Towards Industrial Applications

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Aluminum anodizing dyeing is considered one of the most widely applied dyeing technologies today and utilization of dyestuff in the field still follows the ideology of traditional textile dyeing technology. However, the difference between metal and textile in term of materials to be dyed tends to become one of the crucial factors that decide the outcome of the dyeing process. Therefore, the anodization of metal should be attentive and the applicability of additive used in traditional textile industry on aluminum anodizing dying needs to be fully discussed and researched. Hence, further understanding on additives used in aluminum anodizing dyeing so that one can apprehend that there is one factor which influences color strength besides temperature and concentration. Herein we discussed the low voltage anodization process and the influence of the additives in aluminum anodization dyeing.

Keywords: Electrochemical, Alumina, anodization, dyeing, additives.

1. INTRODUCTION

Anodizing is one of the best techniques which produce metal oxides by oxidation of metal surfaces; it can act as coatings that can protect metals in harsh conditions and corrosion. The anodizing has significantly applied for aluminum and its alloys [1]. The superior surface properties and corrosive resistance of alumina films make aluminum products are most viable for a wide range of applications including packaging, architectural and aerospace industries [2, 3]. Most alumina products obtained from electro oxidation or controlled anodizing surface modification using different types of electrolytes with varying the potential or current density.

Sulfuric acid is a foremost medium for the anodizing alumina compare with other electrolytes because it furnishes the best structure of anodic layers at electrode surface [4]. In 1953, Keller et al., proposed a hexagonal cylindrical model [5] which is further followed and modified in many literature [6,7] According to the proposed model, oxidation of aluminum in the sulfuric acid forms as a porous oxide layer, the structure of aluminum oxide is a close packed hexagonal arrangement with a vertical pore to the substrate [8]. The anodizing aluminum oxide is separated from the metal surface by a thin barrier-type layer and this thickness of the layer is depending upon the applied voltage [9].

This anodized aluminum oxide consists of pores that can be colored by electrolytic coloring and dyeing where metal salts such as tin, nickel, cobalt, etc., used as coloring pigments and sometimes organic dyes are used to coloring the anodized aluminum [10–15]. The dyes and additives are electrostatically interacting with the pores and deposited on the surface of aluminum oxide it provides the transparent layer that reflects the color. The additives play a major role while coloring the metal or textile, besides that temperature and concentration. In this study, we mainly focused on the additives used in the dyeing of anodizing aluminum and compare its color strength towards the industrial applications. In the present work, we discussed the low voltage anodization process and the influence of the additives in aluminum anodization dyeing.

2. MATERIALS AND METHODS

2.1. Materials

Aluminum plate (type: 1050, size: 40*50*0.5mm), NaOH, Na_2CO_3, H_2SO_4 (98%), Z701, EVERANOD Black L-01. The ionic additives such as chloride, acetate, sulfate and citric acid and non-ionic additive such as dextrin were used for the experiments.

2.2. Instruments

Direct current power supply (3V, 20A), cooling water circulation device ((0~30℃) model: P-20 Sheng Hsin instruments), Iso-thermal water bath tank ((30℃~99℃) DENG YONG G-20), electronic weight scale (Precisa XS 625M), color measuring instrument (Konica 2500), electro conductivity meter (SUNTEX SC-2300(0μ s/cm~200ms/cm)).

2.3. Pre-treatment

Aluminum plate is immersed into the solution of 40% NaOH (W/W %) and Na_2CO_3 20g/L at 55˚C for 3 minutes to eliminate the metastable aluminum oxides at the electrode surface and rinse with the doubly distilled water several times to remove the excess alkali. Then it was immersed in 20% HNO_3 (W/W %) solution for 30 minutes to neutralize the electrode and again rinse with doubly distilled water. After the pre-treatment process the electrode was tried and used for further studies.

2.4. Color measurement

There are variety color measurement sources available besides sunlight which is the environment color measurement for naked human eyes and it can be easily analyzed. However, it is accurate measurement for differentiate the colors, since recently several artificial light sources are developed. Light sources can be different in everywhere and one will end up with different measuring results.

1. Type A light source: it is also called tungsten light sources (absolute temperature is approximately 2854 K)
2. Type C light source: it is the light reflected by white cloud at 45 degree elevated angle in the north direction; however, it has been gradually replaced by light source D65(absolute temperature is 6740 K)
3. Light source D65 is similar to average of natural sun light (absolute temperature is 6500 K), which has been used the most on color matching.
4. Light source F is the light emitted by florescence light bulb

2.5. Definition of color strength

The color strength is defined as the ability to impart color to other materials. The color strength is directly depending on the absorption coefficient (K) of colorant. The color strength can be calculated from the ratio between absorption rate of standard and absorption rate of sample. The following equation was used for the calculation of color strength.

$$K/S\ (Batch)/K/S\ (Std.) *100= Batch\ Strength$$

Where $K/S = [\{(1-R)^2/2R\}]$, R is the reflectance, K is absorbance and S is the scattering.

2.6. Electroconductivity measurement

The dyestuff can be divided into three different categories: cationic, anionic and disperse. Different types of dyestuff will create different electroconductivity dissolving in water as solution. Therefore, the effective dyeing tells whether there is a relationship between dyeing efficiency and electroconductivity by examining the measurement of electroconductivities through electroconductivity meter.

3. RESULTS AND DISCUSSION

3.1. Anodization of aluminum and dyeing

The pre-treated aluminum plated was immersed in the 20% H_2SO_4(W/W %) at 20^0C and pass the current of density 1.3 A/dm^2 for 30 minutes, the total potential of this anodization should not goes beyond 3V. Initially all water molecules in electrolytes are adsorbed on the surface of aluminum metal, where it dissociated to form aluminum hydroxide ($Al(OH)_3$) and further it oxidized to form aluminum oxide. Generally, aluminum is very sensitive to moisture hence it is easily form Al^{3+} at the electrode surface and forms a hydrolysis product of its hydroxide. The layer thickness and pore size of aluminum oxide can be altered by adjusting the temperature and reaction times. Fig. 1 shows the schematic diagram of aluminum oxidation where the electrolyte playing a very important role to modify the structure of aluminum oxide. So far sulfuric acid and phosphoric acid used as an electrolyte for aluminum anodization in which sulfuric acid furnishes best structural layers on aluminum surface [4]. The surface charge on oxidized aluminum electrode provides the electrostatic interaction with counter ions hence the reactive dyes are used to coloring the anodized aluminum.

Figure 1. The schematic representation of aluminum anodization and dyeing.

Here we used EVERANOD Black L-01 dye for coloring the alumina, wherein the anodized aluminum electrode was immersed in the dye solution with various additives such as acetate, chloride, dextrin, citric acid and sulfate. The surface charge and pores of aluminum oxide provides the best platform to adhere the dye on the electrode surface. The different additives furnish the smooth layer of dye at the surface of anodized aluminum electrode shown in fig.1. Heating the dyed hydrated Al_2O_3 removes part of the water of hydration, thus forming a denser film which seals in the dye or sealing agent can be added. In this study we have used a sealing agent Z701, after dyed aluminum plate is immersed in the solution contains sealing agent with concentration of 5g/L for 15 minutes at 70°C. This dye modified aluminum electrode was used to further studies to evaluate the influences of different additives in dyeing.

3.2. Effect of additives on different dyeing time

Immerse the anodized aluminum plates into dyeing solutions of concentrations 1g/L and 5 g/L at temperature of 55℃ in dyeing time 1, 2, 3, 5, 10 and 15 minutes respectively followed by rinsing, sealing and drying afterwards, analyze the color strength data obtained by color measuring instrument with computer statistically to find out the relations and trends. Concentration of additives: 1g/L (0.75 g of dyestuff with 0.25 g of additives to make 1 L of the solution), 5 g/L (4 g of dyestuff with1g of additives to make 1 L of the solution). After addition of different additives into the dye solution in the stage, color strength is determined by color measuring instrument. The results are obtained in different concentration as shown in Table 1 and 2.

In this study the dyeing time of three min is kept constant as standard where blank shown the color measurement value is 100, we assume that color strength without any additives is 100%. The color strength increases while increase the dyeing time we analyzed the color strength of different additives in 3 min. Wherein we found the better results for chloride ion compare with other additives however dextrin and acetate shows moderate color strength it can be scale with chloride but the citric acid shows very low color strength.

Table 1. The influences of different additives on color strength with the concentration of additive of 1g/L.

The influences of different additives on color strength with the concentration of additive of 1g/L.						
time (min) types	1	2	3	5	10	15
Blank	41.465	67.833	100	142.083	284.229	409.634
Dextrin	39.828	75.514	107.305	169.953	302.849	450.972
Chloride	39.806	81.912	117.452	174.258	361.813	478.213
Sulfate	34.007	48.118	76.869	135.215	216.824	326.816
Acetate	45.657	74.404	106.563	177.093	322.15	433.13
Citric acid	6.983	8.651	9.648	11.853	13.646	16.214
Standard: assume color strength without additives is 100% Note blank means no additives added						

The obtained results from table are plotted as graph (Fig. 2) where the time with respect to the color strength for better understanding. Increasing the dyeing concentration leads the restriction of ions movement in dyeing bath, because the ionic species interaction is minimized in higher concentration. In this medium also chloride ion act much well than other additives. Here citric acid follows reverse color strength while increase the dyeing time for the reason that bulky group of citric acid restricts and block the pores in anodized aluminum surface which reduces the dyeing at higher concentration even increasing the dyeing time. The obtained values are plotted as graph and shown in Fig. 3.

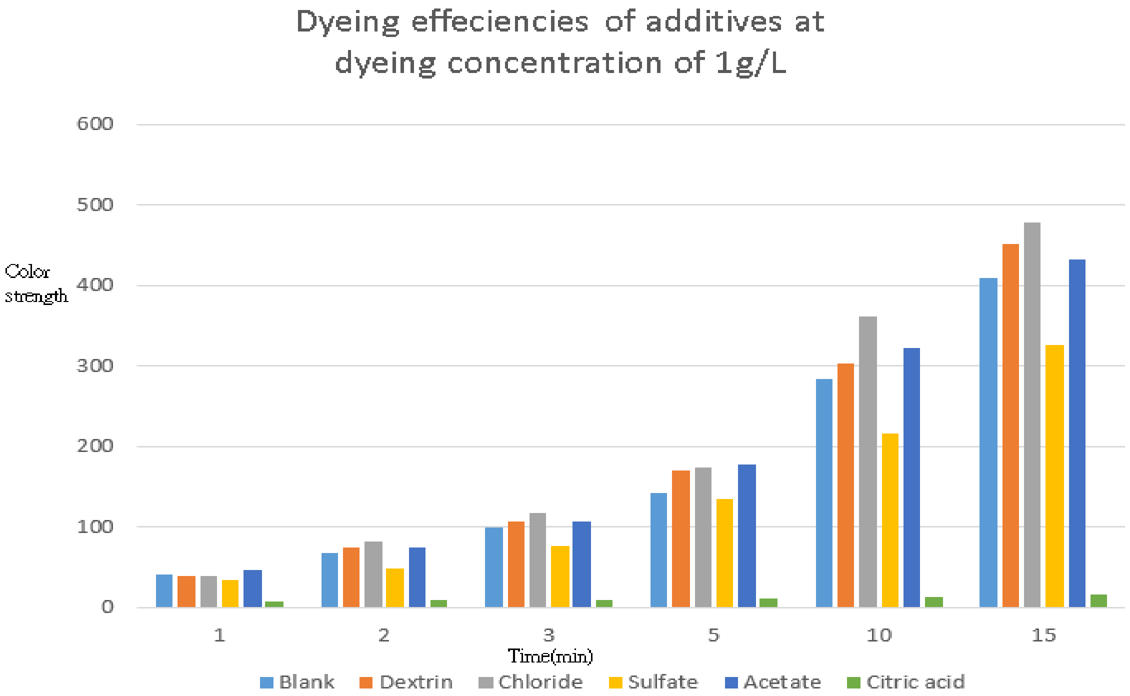

Figure 2. The dyeing efficiencies of different additives at dyeing concentration of 1g/L where 3 mins used as standard for blank.

Table 2. The influences of different additives on color strength with the concentration of additive of 5g/L.

The influences of different additives on color strength with the concentration of additive of 5g/L.						
time (min) / types	1	2	3	5	10	15
Blank	36.551	68.726	100	162.728	231.575	263.324
Dextrin	36.612	72.936	95.966	137.299	217.1538	263.712
Chloride	48.399	85.895	119.065	166.318	247.6695	290.467
Sulfate	22.989	41.52	61.858	98.445	167.447	222.6906
Acetate	49.088	76.871	113.046	186.137	244.963	292.517
Citric acid	2.206	2.334	2.028	1.484	1.211	1.181
Standard: assume color strength without additives is 100% Note blank means no additives added						

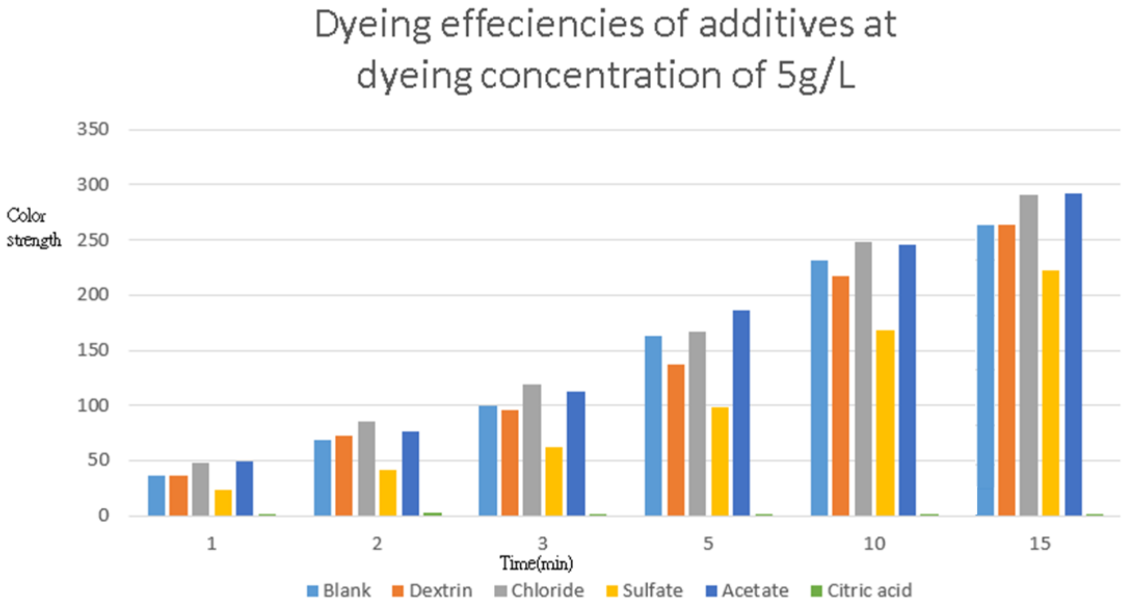

Figure 3. The dyeing efficiencies of different additives at dyeing concentration of 5g/L where 3 mins used as standard for blank.

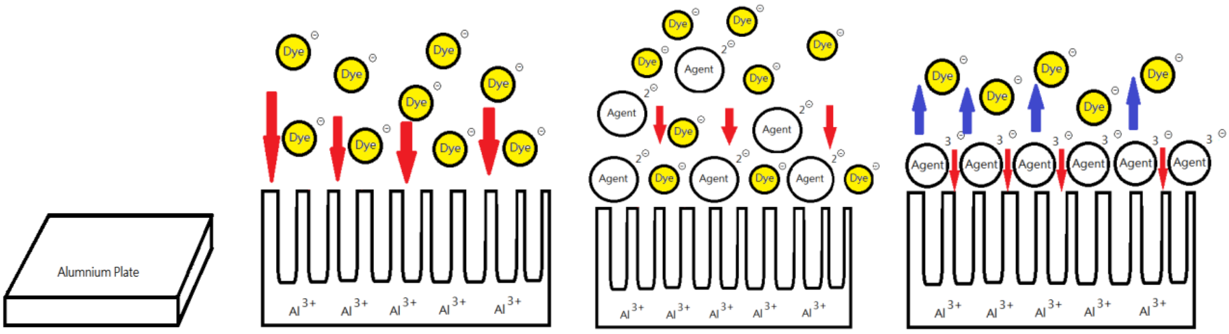

Figure 4. The schematic representation of additives interaction with dyeing of anodized aluminum.

In Fig. 4 the blank, only dyes remain without any additives hence it easily diffuses from the bulk to the electrode interface and easily occupies the pores in anodized aluminum surface but the dyeing efficiency is poor without the presence of additives and the color fading also high. So it can be proceeding with different additives where additives act as carrier to take the dye molecule to the electrode surface but the some of additives shows negative effect due to the bulkiness and steric effect. These bulk additives are block the pores in electrode surface and let the dyes out from the aluminum surface.

3.3. Effect of additives on its ionic conductivity

In the sector of industry, additives can be divided into two categories: ionic and non-ionic. The experimental groups designed for the research are as the following: (1) ionic type: chloride, acetate, sulfate and citric acid (2) non-ionic type: dextrin. The above two groups are discussed in the following sections where the ionic conductivity meter is used to measure the ionic conductivity and this experiment monitor the influence of ionic conductivity on different additives in dyeing of anodized aluminum. The ionic conductivity plays a vital role in dyeing, the color strength is increasing while increasing the ionic conductivity of dyeing bath, and therefore the additives are employed in dyeing. From the Table 4 and 5, we conclude the color strength depends on the various additives by its ionic conductivity.

Table 4. The relationship between color strength and ionic conductivity in 1g/L dye solution with different additives

Test item	Pure water	**Concentration of dye solution: 1g/L**					
		Black	Sulfate	Dextrin	Chloride	Citric acid	Acetate
pH before adjustment	7.3	7	6.9	6.9	6.9	4.6	6.9
Electro-conductivity before measurement	221	637	985	636	1109	578	862
pH after adjustment	5.5	5.5	5.5	5.5	5.5	5.5	5.5
Electro-conductivity after measurement	217	636	981	981	633	1107	860
Trent of color strength	–	STD	↓	↑	↑	↓	↑
Note: 20% acetic acid solution was used to adjust the pH Note: blank means no additives added							

Based on basic dyeing theory, the color strength is enhanced in rising ionic conductivity of dye solution by addition of salts. Before the experiment, dyeing bath in adjusted to the pH 5.5 which is optimized for good efficiency in dyeing this dye on anodized aluminum, 20% acidic acid was used to adjust the pH of the solution. Here blank take as standard and compare the conductivities of different additives, among all the chloride ion shows higher ionic conductivity hence it shows good dyeing efficiency which is also confirmed in above experiment.

Table 5. The relationship between color strength and ionic conductivity in 5g/L dye solution with different additives.

Test item	Pure water	**Concentration of dye solution: 5g/L**					
		Black	Sulfate	Dextrin	Chloride	Citric acid	Acetate
pH before adjustment	7.6	6.8	6.9	6.7	6.9	4.1	7
Electro-conductivity before measurement	218	1249	2880	1243	3490	1157	2350
pH after adjustment	5.5	5.5	5.5	5.5	5.5	5.5	5.5
Electro-conductivity after measurement	216	1246	2870	1240	3480	2250	2340
Trent of color strength	–	STD	↓	=	↑	↓	↑
Note: 20% acetic acid solution was used to adjust the pH Note: blank means no additives added							

3.4. Ratification by statistic

The JMP statistical software from SAS was used here to ratify the experimental data and allow understanding the rationality of the whole experiment and confirming the major factors at the same time.

Table 6. The relationship of color strength (here, 0~0.3: a little related 0.3~0.7: somewhat related 0.7~1.0: highly related), dying time and concentration.

	Strength	Time	Concentration
Strength	1	0.7245	-0.1685
Time	0.7245	1	0.0458
Concentration	-0.1685	0.0458	1

Table 6 reveals that dyeing time and color strength are directly proportional: the longer the dyeing time, the stronger the color strength.

Table 7. Analysis on the experimental result

Summary of Fit	
R^2	0.980549
R^2 Adj	0.973943
Root mean square error	19.83379
Mean of response	132.4693
Observations (or Sum of Wgts)	72

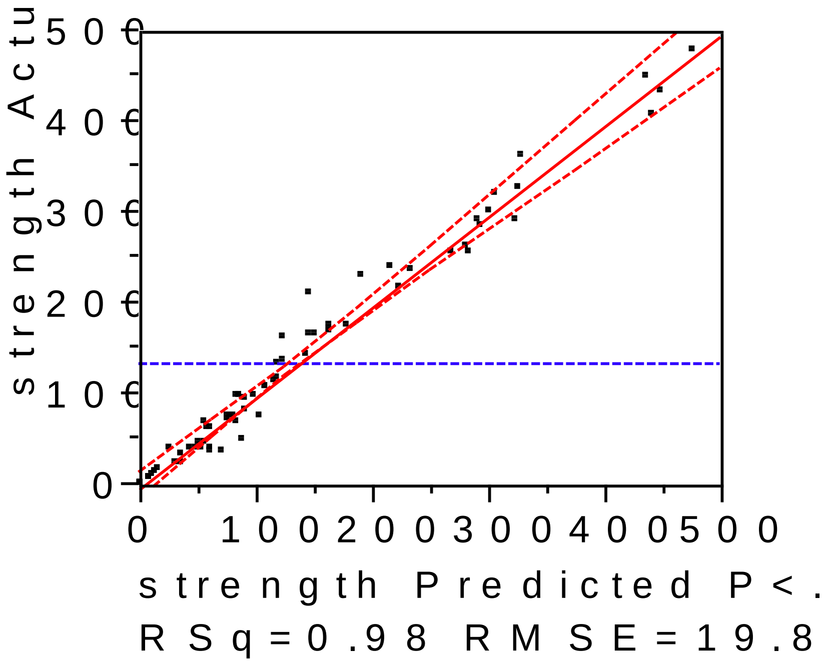

Figure 5. Plot trend based on the experimental results.

Based on data collected from the experiment designed and confirmed by software" JUMP", as shown in table seven and Fig. 5, R^2 was computed. The value of R^2 is 0.98 (normally, if R^2 is larger than 0.7, it means that the experiment is reliable).

4. CONCLUSION

The research can be a valuable reference for industries that apply aluminum anodizing dyeing technique. In conclusion, the dyeing efficiency can be altered by addition of various additives. In order to increase the color strength, additive such as chloride or acetate should be added for the best result; on the other hand, if one intends to have a nice, even dyeing result, additive such as sulfate is preferred. In any cases, the dosage of additives can be adjusted since each user has different operational condition. Based on this research, one learns that coloring efficiency can be increased by rising ionic conductivity for some additives but selection of additives need to be done in a cautious manner because some salts with bi-protons and multi-protons can bring up the electro conductivity but unable to enhance the dyeing efficiency and color strength. The possible reason for this due to the interaction between multi-proton ions and positive charge on the surface of the aluminum plate; consequently, the positive charge on the surface of the aluminum plate decreases and make aluminum surface less attractive to the dyestuff. Other possible reason may be due to the "hindering effect" of multi-proton ion on the surface of the aluminum plate which also makes dyestuff difficult to bond with the aluminum ions and eventually reduces the dyeing efficiency.

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