



98 (4), 22-28 (July 2011)

A Protective Decorative Electrolytic Coloring Process for Aluminum

by M. Reda Gad Abu El-Magd[∗] National Research Centre Dokki, Cairo, Egypt

ABSTRACT

The main task of this work was to study the influence of the different parameters on the electrolytic coloring process for aluminum, including plate quality (appearance, adhesion, thermal stability), coating color, coating thickness, coloring time, agitation, electrode material, AC voltage, concentration of organic additives and surface topography. Independent of the coloring method used, the results have shown that the applied AC voltage and time of treatment influenced the character of the coloring process under the conditions studied, and additives enabled us to achieve color uniformity and to expand color and shade selections. It was concluded that adhesion and thermal cycling tests indicate the durability of the coating. The maximum coating thickness obtained with a process based on sodium benzene sulfonate is sufficient for decorative applications. Finally, the surface morphology was characterized by scanning electron microscopy (SEM).

Keywords: aluminum, anodizing, coatings, additives, electrolytic coloring, surface topography

Introduction

One of the most widely used coloring methods for the past decades is electrolytic coloring (EC). Electrolytic coloring is a viable method of producing an interesting range of beautiful colors available for architectural, decorative, space, industrial and aerospace applications.¹⁻⁶ Many methods for EC of aluminum have been widely used in recent years.⁷⁻¹³

Among various preparation methods, EC processes in the presence of silver nitrate solutions have not been extensively investigated. However, a major problem of this process is poor color reproducibility. To solve this problem, many related improvements have been attempted by controlling certain parameters of the EC process such as the coloring time, ^{9,10,14} the additive concentration, ^{15,16} AC voltage^{9,14,17,18} and so on. Nonetheless, despite efforts to tightly control the EC process, variation in the color is more or less unavoidable.

Small amounts of additives in the coloring process have been used to stabilize, accelerate or decrease the coloring rate and also have significant effects on the deposit characteristics such as brightness, grain size, hardness, ductility and internal stress.^{15,16,19,20} However, it must be noticed that additives such as heterocyclic organic compounds on the EC process for anodized aluminum have a positive influence on the color intensity, color uniformity of the probes and the throwing power of the salt solutions.^{8,9,12,16}

Although there have been numerous studies on the EC of aluminum, the synergistic effect of some organic additives is still not well understood. The technology of aluminum is the most evolved of the common metal technologies.^{21,22} The EC of anodized aluminum makes the aluminum surface hard, durable, attractive and resistant to corrosion and erosion.

Anodizing is used widely in the surface treatment of aluminum alloys for aerospace applications and protection.^{1,4} Anodization is one of the most important processes in corrosion protection and color finishes for aluminum.²³⁻²⁵ Aluminum is a very active metal that forms a natural impervious oxide, which must be removed before plating.²⁶ In the anodizing of aluminum, the aluminum

*Corresponding author:

M. Reda Gad Abu El-Magd Professor of Metallurgical Engineering Chemical Engineering and Pilot Plant Department National Research Centre Dokki, Cairo, Egypt Phone: 002023371499 Fax: 002023370931 E-mail: dr reda gad@yahoo.com





98 (4), 22-28 (July 2011)

workpiece is the anode and graphite or aluminum is used as the cathode. During electrolysis, the oxide or hydroxide precipitated within the pores colors the film as brown, bronze, blue, yellowish gray or black, depending on the salt solution and the AC voltage employed.^{11,14}

In this work, assessment of coating quality included measurements of adhesion and thermal stability by the tests to be described, in addition to evaluation of appearance. This article describes the various effects of organic additives on the properties of electrolytically colored anodized layers in the presence of silver nitrate salts.

Experimental

In our study of electrolytic coloring (EC) of aluminum, test specimens 0.1 mm thick having a total surface area of 20 cm² were used. Chemical analysis of the test specimens indicated 94.66% aluminum and 5.17% silicon. The composition of the EC bath is listed in Table 1. The specimens were given the following pretreatment: degreasing in acetone and calcium carbonate and chemical polishing. Cold and hot rinses were used after each of the above steps.

yao ooloriing baan.
0.5 g/L
10,15,20 V
5,10,15,20 min
25°C
5.4
Graphite electrode

Table 1 - Electrolytic coloring bath

Aluminum specimens were subjected to a primary anodizing treatment in 10% sulfuric acid solution. The aluminum was then subjected to a secondary electrolytic coloring treatment containing a metal salt. This work was developed by Tsangaraki-Kaplanoglou, *et al.*^{8,9} After the EC process, the specimens were rinsed thoroughly in deionized water, dried in a stream of air at room temperature and stored in a desiccator.

The additives employed were: sodium benzene sulfonate, sodium p-toluene sulfonate and sodium 2-naphthalene sulfonate. The concentrations of these additives were varied from 0.25 to 1.00 mg/L in an electrolytic solution of the coloring bath using anodized aluminum as the cathode and graphite as a counter electrode. These conditions seemed to be suitable because higher or lower values gave negative results.

The samples were weighed before and after the plating cycle. The differences between the two weighings allowed calculation of the effective coating thickness after coloring deposition, rinsing and drying. The specimen surfaces were examined by scanning electron microscopy (SEM) to investigate the surface topography of the deposit. Assessment of coating quality included measurements of adhesion and thermal stability by the tests described next, in addition to appearance.

Adhesion bend test

Adhesion can be classified in a minimum of three categories: excellent, intermediate and poor. The intermediate class is most often subdivided into the classes of good and fair. A destructive method has been developed for determining the quality of adhesion bending. The test specimens were bent repeatedly through an angle of 180° until rupture occurred. Following fracture, no detachment of the coating should be observed by probing with a sharp instrument. If such separation is observed, adhesion is considered unacceptable. Also, cracks in the basis metal or plating were not considered to be a failure unless accompanied by flaking, peeling or blistering.

Thermal stability test

A thermal stability or thermal cycling test was used to determine both the coating's ability to withstand high temperatures and its adhesion to the basis metal. This test was carried out by heating the panels in an electric oven to 280°C within 30 min and maintaining them at that temperature for the next 8 hr, then allowing the panels to cool at room temperature overnight. This test was carried out for 12 consecutive days, and the appearance was observed for color, peeling, blistering and cracking. Any





98 (4), 22-28 (July 2011)

resulting discoloration would indicate poor thermal stability of the coating due to thermal decomposition of the coating constituents.

Results and discussion

The properties of the coating were found to be important in characterizing the nature of the electrocolored anodized layer and in support of the results of the plate quality tests as well. Many parameters were noted during the coloring process which affect the coloring quality.

Influence of agitation

Agitation using a magnetic stirrer during deposition (coloration) was kept constant at 500 rpm, which was sufficient to ensure uniformity of temperature and concentration. This rate of agitation was believed to give a more even deposit, especially on components that have intricate shapes. Excess agitation should be avoided.

Agitation or rotation during the process is useful so that gas will not be trapped during coloring. It was found that stirring an electroplating bath may increase, decrease or not affect the deposition rate.⁶

The effect of agitation on the coating thickness of EC bath is shown in Table 2. It can be concluded that the dependence of deposition rate on bath agitation type and magnitude seems to have no appreciable effect on EC process.

Table 2 - Effect of agitation of coating thereas.						
Agitation	Agitation speed	Coating thickness, g/m²				
Mechanical	0	6.50				
	50	6.41				
	75	6.47				
	100	6.54				
Magnetic	Low	6.45				
	Medium	6.51				
	High	6.58				
Ultrasonic		6.63				

Table 2 - Effect of agitation on coating thickness.*

*Reference bath: AC voltage, 15 V; Coloring time, 10 min; Temperature, 25°C; pH 5.4; Additive, 0.50 mg/L

Influence of plate quality

Appearance. The final appearance of the EC-processed article is related to the surface finish of the article before the porous layer of alumina is formed during anodization. On a brilliant or glossy specimen, the color effects obtained by the process are brilliant, whereas on a dull or matte object, the color effects are dull or matte.

The as-plated deposits from test baths containing different types of organic additives were either very bright, bright, semi-bright or weak over the range of additive concentrations tested in the coloring bath. By increasing the concentration of additives and AC voltage up to 15 V, a mottled and patchy appearance occurred, as shown in Table 3. The formation of bright deposits was attributed to the adsorption of these ions on certain growth steps. Better, attractive and decorative appearance was obtained with deposits from sodium benzene sulfonate.





98 (4), 22-28 (July 2011)

AC	Additive	Sodium benzene sulfonate			Sodium p	-toluene si	ulfonate
Voltage, V	concentration, mg/L	Appearance	Coating color	Color uniformity	Appearance	Coating color	Color uniformity
10.0	0.25	В	WB	N,R	W	WB	N,R
	0.50	В	CB	H,R	S	LB	H,R
	0.75	S,P	MB	H,R	S,P	NB	H,I
	1.00	W	LB	H,I	S,M	MB	N,I
15.0	0.25	V	AB	H,R	S	В	N,R
	0.50	V	DB	H,R	В	LB	H,I
	0.75	В	DB	H,R	S,M	NB	N,I
	1.00	В	NB	H,R	W,P	SB	N,I
20.0	0.25	S	PB	N,R	S,M	PB	N,R
	0.50	B,P	LB	N,I	S,M	NB	N,I
	0.75	S,M	NB	N,I	W,P	SB	N,I
	1.00	W	SB	N,I	W,M	WB	N,I

Table 3 - Effect of organic additives on coating appearance and color at a coloring time of 10 min.

Appearance: B = bright; M = mottled; P = patchy; S = semi-bright; V = very bright.

Coating color: AB = amber bronze; CB = canary bronze; DB = dove bronze; LB = light bronze; MB = medium bronze; NB = near bronze; PB = pale bronze; SB = slightly bronze; WB = weaker bronze.

Color uniformity: H = homogeneous; I = irregular; N = non-homogeneous; R = regular.

Adhesion bend test. The adhesion was satisfactory and can be improved by heating at 400°C for 10 min. The coatings were found to possess good adhesion with no peeling from the substrate. This indicated extremely adherent coatings. The adhesion test also showed that deposits from baths with the sodium 2-naphthalene sulfonate additive were more brittle than those from the other organic additives. Brittleness is not indicative of bad adhesion in that even brittle coatings could not be peeled with a hard knife. Similar results were observed by Kuhm, *et al.*²⁵

Thermal stability test. It is interesting to note that no discoloration of the coating was observed after the 12-day thermal cycling test. This also shows the durability of the coating when used in higher temperature electronic applications, and the coating has a decorative appeal as well.

Influence of coating color

The color could be changed according to the time of treatment and the applied AC voltage. The color of the coating and color uniformity are shown in Table 3.

One of the principle objectives in this study was to find the influence of coating color. The color is used as quality check on the thickness. The quality and appearance of the coatings were good. This work is agreement with Takenaka, *et al.*¹³ and Karagianni and Tsangaraki-Kaplanoglou.¹⁶ The color of the coating obtained for the organic additives studied at various concentrations and AC voltages can be found in Table 3, and at various coloring times in Table 4.

From a practical point of view, the different color tones ranging from amber to light bronze and dove to weak bronze were dependent on the duration of the electrolysis, and the organic additives as shown in Table 3. This work was developed by Karagianni and Tsangaraki-Kaplanoglou,¹⁶ who have reported that the color and depth of the shade produced depend on the metal being deposited and the coloring conditions used. Our data agree with the results reported by Cheng, *et al.*,¹⁷ who demonstrated that the color of coatings depends on the coloring time, current density, concentration of additives and applied AC voltage.

The quality of the coatings was surprisingly good and they exhibited a satisfactory appearance. However, the colors obtained lacked the vividness and reflectivity associated with decorative finishes obtained from electrolytic processes. The coloration of





98 (4), 22-28 (July 2011)

the product was nonetheless attractive, uniform and reproducible and the color did not fade over the long term. The reproducibility of the color tone was very high. These results are consistent with the work of Golubev, *et al.*⁶

Coloring	Sodium I	benzene su	lfonate	Sodium p-toluene sulfonate			Sodium 2-r	apthalene	sulfonate
time, min	Appearance	Coating color	Color thickness, g/m ²	Appearance	Coating color	Color thickness, g/m ²	Appearance	Coating color	Color thickness, g/m ²
5	В	MB	5.3	S	WB	4.5	W	WB	3.7
10	V	DB	6.2	В	NB	5.1	S	MB	3.9
15	B,P	CB	6.8	S,M	PB	5.5	W,M	SB	4.3
20	B,M	NB	7.2	W,P	SB	5.9	W,P	PB	4.7

Table 4 - Effect of coloring time on coating thickness with organic additives at a concentration of 0.50 mg/L and AC 15 V.

Appearance: B = bright; M = mottled; P = patchy; S = semi-bright; W = weak; V = very bright.

Coating color: CB = canary bronze; DB = dove bronze; MB = medium bronze; NB= near bronze; PB = pale bronze; SB = slightly bronze; WB= weaker bronze.

Influence of coating thickness

Coating thickness was controlled by adjusting the time or the bath temperature to produce a desired deposition rate. This was found to be more satisfactory during periods of sustained operation as the bath temperature could be maintained at a constant 20°C, enhancing the uniformity of the entire processing sequence.

The thickness of the coating obtained for organic additives at various concentrations and AC voltages can be found in Table 5, and at various coloring times in Table 4. Results show that the maximum coating thickness is about 6.2 g/m² in the case of 0.50 mg/L sodium benzene sulfonate at 15 V, and a 10-minute coloring time, which is sufficient for decorative applications. The results obtained were in agreement with those of Shih and Huang.⁷ It was found that the coating thickness increased with increasing coloring time as shown in Table 4, and similar results were reported by Golubev , *et al.*⁶

AC Voltage, V	Additive concentration, mg/L	Sodium benzene sulfonate	Sodium p- toluene sulfonate	Sodium 2- napthalene sulfonate
	0.25	4.6	4.0	3.3
10.0	0.50	5.3	4.5	3.7
	0.75	4.4	3.8	2.8
	1.00	4.0	3.2	2.0
15.0	0.25	5.6	4.2	3.5
	0.50	6.5	5.1	3.9
	0.75	5.2	4.0	3.2
	1.00	4.8	3.5	2.5
20.0	0.25	4.3	3.6	2.8
	0.50	4.7	3.9	3.1
	0.75	3.7	2.9	2.2
	1.00	3.0	2.3	1.9

Table 5 - Effect of organic additives on coating thickness at a coloring time of 10 min.

For any set of conditions, the color can be used as a quality check on the thickness. The uniformity in both thickness and color is improved if the aluminum is treated with a slight etch prior to the conversion coating. In the case of the severely heat-treated and cast materials, a good etch is almost essential to good coating.²⁷





98 (4), 22-28 (July 2011)

Influence of electrode material

The appearance and color of the coating developed in the case of 0.50 mg/L sodium benzene sulfonate additive, for 10 min at an applied AC voltage of 15 V at room temperature (25°C) depends on the electrode material. The coating color is dependent on the quantity of deposit material and the nature of the auxiliary electrodes used. It was indicated that uniform colors of greater depth could be obtained by using a counter electrode of the same metal as the metallic salts in the coloring bath. With titanium electrodes, the deposition rate is several times less than with graphite or stainless steel electrodes. This phenomenon was addressed by Tsangaraki-Kaplanoglou, *et al.*,^{8,9} and our results are in accord with their work.

Surface topography

Scanning electron microscopy (SEM) is a means of visualizing the morphology of a surface at a high magnification and with a high depth of field. The appearance of the surface topography strongly depends upon the characteristics of EC bath, which has achieved some attention with respect to structures such as the works of Kuhm, *et al.*,²⁶ Dasquet, *et al.*²⁸ and Aiwaka, *et al.*³¹ However, only scant attention has been paid to the effects of organic additives on the surface topography of deposits, such as the work of Thompson, *et al.*⁴ and Tsangaraki-Kaplanoglou , *et al.*^{8,9}

In our prior work,¹⁷ electron micrographs of plates from organic additives at various coloring times, voltages and additive concentrations at 25°C were prepared. Major differences in distribution were observed for different color finishes, depending on the solution of additives.

Influence of coloring time. In general, aluminum coatings colored for 10 min, at an additive concentration of 0.50 mg/L, and 15 V contained a number of large uniform regular pores. Increasing the coloring time to 20 min caused the formation of a coarse, non-uniform irregular structure. The shape of the pores was altered, and a gradual decrease in pore size and number was observed with increased coloring time for all additives. This observation is in accord with prior studies.⁷⁻¹⁰ From previous studies of organic additives, it was found that the deposit from the solution containing sodium benzene sulfonate seemed to have the decorative appearance depicted in Table 4.

Influence of AC voltage. The deposit produced from the solution containing sodium benzene sulfonate at 10V, an additive concentration of 0.50 mg/L, and a coloring time of 10 min exhibited greater homogeneity, was dense and smooth, and the grains were regularly shaped and uniformly distributed. By increasing the voltage to 20 V, the grains of the deposit became very large, non-homogeneous and irregular as described in Table 3. In general, the study of the three additives showed that the character of the grain boundaries in the coating layers from the solution containing sodium benzene sulfonate differed from the other additives. This conclusion is in exact accordance with prior work.^{7,15,17,18}

Influence of additive concentration. It can be clearly seen that, the deposits from solutions containing the low sodium benzene sulfonate concentration (0.25 mg/L), at a coloring time of 10 min and at 15 V, had a coarser, more uniform pore structure with a larger grain size than at higher concentrations (1.00 mg/L). However, deposits at low additive concentrations showed that the coating films had homogeneous, regular grain shapes and attractive appearance as represented in Table 3, indicating that the coating showed good durability. Our work is in agreement with Tsangaraki-Kaplanoglou, *et al.*⁹ In contrast, at high additive concentrations, a small number of partially spotted particles and nonuniform pores distributed on the surface were obtained.

The examinations of deposit cross sections showed that the type of organic additive and its concentration affected the structure of the coating layers. It would be expected that the effect of additives should lead to a means of accelerating the reaction rates of the electrolytic coloring bath. Our data agree with the results reported by Karagianni and Tsangaraki-Kaplanoglou.¹⁶

Conclusions

Analysis of the data has led to the following conclusions:





98 (4), 22-28 (July 2011)

- The electrolytic coloring process was found to depend on the aromatic character of the additive, the position of the organic group in the molecule, and on the number of carbon atoms in their rings. The coatings produced were found to possess good adhesion to the substrate and can be used in high temperature environments.
- The coloration of the product is uniform and reproducible, and the color did not fade over the long term. The color could be changed by regulating the time of treatment and the applied AC voltage.
- The appearance and color of the coating depend on the electrode material and agitation has no appreciable effect in this process.
- Scanning electron micrographs of the colored coatings demonstrate the incorporation of silver metal in the pores of the anodically oxidized film of aluminum, providing a wide range of color tone.

References

- 1. X. Zhou, P.G. Sheasby & B.A. Scott, in *Shreir's Corrosion, Volume 4*, Elsevier, B.V., Maryland Heights, MO, 2009; pp. 2503-2518.
- 2. Y. Toshev, et al., Proc. 2nd Inter. Conf. on Multi-Material Micro-Manufacture, W. Menz, S. Dimov & B. Fillon, Eds., Elsevier B.V., Maryland Heights, MO, 2006; pp. 323-326.
- 3. E. Stoyanova, et al., Trans. Inst. Met. Fin., 82 (5/6), 157 (2004).
- 4. G.E. Thompson, et al., Aircraft Eng. and Aerospace Tech., 71 (3), 228 (1999).
- 5. A. K. Sharma, et al., Metal Finishing, 95 (12), 14 (1997).
- 6. A.I. Golubev, E.P. Rogozhina & N.E. Kurbatova, Zashchita Metall., 24 (5) 673 (1989).
- 7. H.H. Shih & Y.C. Huang, Mat. Proc. Tech., 208 (1-3), 24 (2008).
- 8. I. Tsangaraki-Kaplanoglou, et al., Surf. Coat. Technol., 200 (12-13), 3969 (2006).
- 9. I. Tsangaraki-Kaplanoglou, et al., Surf. Coat. Technol., 201 (6), 2749 (2006).
- 10. M. Zemanová, et al., Renewable Energy, 33 (10), 2303 (2008).
- 11. S. Yongqing, Metal Finishing, 98 (12), 61 (2000).
- 12. S. Yongqing, et al., Metal Finishing, 97 (12), 8 (1999).
- 13. T. Takenaka, H. Habazaki & H. Konno, Surf. Coat. Technol., 169-170, 155 (2003).
- 14. E. Kikuti, et al., J. Braz. Chem. Soc., 15 (4), 472 (2004).
- 15. Th. Dimogerontakis & I. Tsangaraki-Kaplanoglou, Thin Solid Films, 402 (1-2), 121 (2002).
- 16. B. Karagianni & I. Tsangaraki-Kaplanoglou, Plating & Surface Finishing, 83 (9), 73 (1996).
- 17. Z. Cheng, et al., Surf. Coat. Technol., 202 (17), 4102 (2008).
- 18. J. Zhang, et al., Trans. Inst. Met. Fin., 83 (2), 95 (2005).
- 19. N. Kallithrakas-Kantos, et al., Thin Solid Films, 326 (1-2), 166 (1998).
- 20. R. Moshohoritou, I. Tsangaraki-Kaplanoglou & C. Kotsira, Plating & Surface Finishing, 81 (1), 60 (1994).
- 21. M.Z. An, L.C. Zhao & Z.M. Tu, Mat. Chem. Phys., 77 (1), 170 (2003).
- 22. X. A. Ventura, Proc. SUR/FIN 1996, NASF, Washington, DC, 1996; pp. 1011-1024.
- 23. I. Tsangaraki-Kaplanoglou, et al., Surf. Coat. Technol., 200 (8), 2634 (2006).
- 24. L. Li, Solar Energy Mater. Solar Cells, 64 (3), 279 (2000).
- 25. P. Kuhm, et al., U.S. Patent 5,587,063 (1996).
- 26. F.A. Lowenheim, Electroplating, McGraw-Hill, New York (1978) p. 89.
- 27. E.A. Groshart, Metal Finishing, 82 (6), 69 (1984).
- 28. J.P. Dasquet, et al., Thin Solid Films, 371 (1-2), 183 (2000).
- 29. K. Aikawa, S. Ishikura & M. Kato, U.S. Patent 5,849,169 (1998).

About the author

Dr. M. Reda Gad Abu El-Magd is a Professor of Metallurgical Engineering in the Chemical Engineering and Pilot Plant Department at the National Research Centre in Dokki, Cairo, Egypt.