

## INTEGRAL COLOUR ANODISING OF ALUMINIUM USING ALTERNATING CURRENT

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## ABSTRACT

Integral colour anodising of aluminium is carried out by the constant voltage process using alternating current (A.C.) in an electrolyte containing 40 g/l sulphosalicylic acid and 40 ml/l formic acid in conjunction with 5-10 g/l pyrogallol, pyrocatechol, p-aminophenol and metol at 25-30°C with operating voltage between 50 and 80 V. Colours ranging from brownish black, yellowish green, brown, reddish brown, purple, chocolate and black are obtained. The colour depends on the composition of the alloy and operating conditions.

**Key words:** Colour anodising, aluminium, alternating current

## INTRODUCTION

One of the most popular anodising processes is integral colouring in which colour is produced during the anodising step itself by the use of special organic acid based electrolytes. This is also called 'self colour' or 'built-in-colour' anodising process wherein extremely weather resistant, hard and light fast coatings are produced on aluminium and its alloys. A wide variety of electrolytic baths have been used for architectural anodising purposes. The colours obtained are dependent on factors such as composition of aluminium alloy, nature of the electrolyte, type of current, thickness of the coating, anodising time, voltage and temperature. Several publications have appeared on various aspects of integral colour anodising [1-7].

Integral colour anodising is carried out using special types of aluminium alloys and/or special organic electrolytes such as oxalic acid [8];

characteristic. The well known Kalcolor [11] and Duranodic [12] process employs direct current for anodising.

The WGX process employs oxalic acid for decorative and architectural anodising and the method adopted was to anodise using alternating current at a constant voltage between 50 and 60V in an electrolyte containing 35 g/l oxalic acid at 28-30°C in order to produce coating of 10-12 µm in one hour. Table I (15) shows an investigation into the a.c. anodising of various aluminium alloys in a 90 g/l oxalic acid at 20°C. It will be noted that various colours are obtained which may be considered of architectural merit.

Superimposed a.c. on d.c. (16) at resonant frequencies in electrolytes containing 100 g/l sulphamic acid, 80 g/l tartaric acid and 3 g/l sulphuric acid gave rise to reduced power consumption and increased colour reproducibility. A.C. has been utilised for integral colouring using 100 g/l sulphoitaconic acid and 5 g/l sulphuric acid at 15-30°C (17). Another

Table I: Colours obtained on various alloys after anodising in 90 g/l oxalic acid, 2.1 A/dm<sup>2</sup>, 20°C, 60 minutes using a.c. [15]

Alloy composition	Time of anodising min	Voltage range	Anodic film thickness (µm)	Colour of coating
99% Al	30	72-78	15	Medium gold
	60	72-92	30	Golden brown
5% Si alloy	60	70-100	22	Greyish yellow
8% Si alloy	60	75-100	20	Dark greyish yellow
Mn 1-1.5, Si 0.6	60	81-91	25	Golden brown
Mg 1.8-2.7, Si 0.6	60	73-96	30	Golden brown
Mg 0.4-0.9, Si 0.3-0.7	15	72-74	6	Pale gold
	30	72-77	14	Medium gold
	45	72-85	20	Dark gold
	60	72-91	25	Golden brown
Mg 0.4-1.4, Si 0.6-1.3 Mn 0.4-1.0	60	70-85	20	Bronze-brown

sulphosalicylic acid + sulphuric acid [9-11]; sulphophthalic acid + sulphuric acid [12]; sulphosalicylic acid + formic acid [13]; citric acid + formic acid [14] and phenol sulphonic acid [7]. The organic electrolytes are formulated into balanced mixtures which have just the correct properties for forming hard porous coatings, normally with a rising voltage

electrolyte [18,19] contains 100 g/l sulphomaleic acid and 5 g/l sulphuric acid. Hungarian process [20,21] is based on 30 g/l formic acid, 50 g/l sulphosalicylic acid and 5 g/l hydroquinone which uses either a.c. or d.c. Pulsed current [22] has been utilised for integral colouring using 80 g/l oxalic acid.

The use of a.c. for anodising 23,24 offers a number of advantages like (a) low capital investment on electrical equipment because step down transformer and variac is utilised in the place of rectifier (b) both electrodes are aluminium and hence anodised simultaneously and (c) electrolyte volume is most efficiently utilised. In this paper the influence of addition agent, operating parameters like current density, temperature and anodising voltage with respect to colour and thickness of the coating are reported.

## EXPERIMENTAL

Aluminium alloy panels of size 75 x 50 mm and extrusions were degreased with trichloroethylene, etched in 50 g/l sodium hydroxide, rinsed, desmutted in 20% v/v nitric acid, rinsed with tap water and then with distilled water. The following alloys were used:

- 2 S or 99% Al
- 3 S with 1.3% Mn
- B 51S with 1.0% Si, 0.9% Mg and 0.7% Mn

They were anodised in an electrolyte of the following composition:

- 5 - sulphosalicylic acid .. 40 g/l
- Formic acid .. 40 g/l
- Pyrogallol, pyrocatechol, p-aminophenol or metol .. 5-10 g/l

Distilled or deionised water was used for electrolyte preparation. The electrolyte was kept in a 5 litre beaker with external cooling arrangement and the temperature was maintained by the circulation of brine water from cooling plant. Air agitation was provided by the use of sintered porous crucible kept at the bottom of the beaker. Current was supplied from 0-270V, 30 A auto-transformer. For anodising, two of the pretreated panels were mounted in an insulated jig and were placed opposite to each other with a gap of 50 mm. No cathode is needed.

After the panels were placed in the electrolyte and the power turned on, the current was raised slowly to the prescribed current density. If the voltage is raised suddenly, excess current flows, resulting in burning of the coating. The voltage was steadily and slowly raised during the initial 5-10 minutes.

Thickness of the coating was measured by stripping the coating in a solution containing 20 g/l chromic acid and 35 ml/l phosphoric acid at 90°C. Thickness was calculated from the formula,

$$T = W/AD$$

where W = weight of the coating; A = Area of the panel in cm<sup>2</sup> and D = Specific gravity (2.5). The colour of the panel was ascertained by visual observation.

## RESULTS AND DISCUSSION

### Effect of addition agent

The colour of the coating obtained from a bath of 40 g/l sulphosalicylic acid and 40 ml/l formic acid is streaky and non-uniform. Hence, addition agents like metol, pyrogallol, pyrocatechol and p-amino phenol were added as stabilizing agent to produce uniformly coloured coatings. The addition agent is found to permit the operation of the bath at higher voltages without the problem of spark discharge. The colour of the coating produced by the use of d.c. is less intense and requires higher voltages to produce the same tone. Optimum concentration of addition agent is found to be 5-10 g/l. Due to the alternate evolution of hydrogen at the electrode surface during anodising the coating is brighter than that of d.c. coating due to the effective cleansing action.

### Effect of sulphate

To improve the conductivity of the electrolyte and thereby bring down the operating voltage required for anodising, addition of sulphate in amounts of 0.5 to 10 g/l were tried. Sulphate in excess of 1 g/l is detrimental to the formation of coloured coatings. Chloride should be eliminated completely; otherwise, as the voltage required for anodising is high, no coating forms but pitting takes place.

### Effect of temperature

Temperature is an important variable which must be considered in the operation of the solution. The recommended temperature should be maintained in order that uniform finish be maintained as the bath is used. The temperature of electrolyte was varied between 15-40°C by keeping the anodising time and voltage constant. When the temperature of the electrolyte was on the lower side (<20°C), dark shades were produced, whereas higher temperature (>30°C) leads to lighter shades. If the temperature of the electrolyte is on the lower side, efficient cooling arrangement is required which is expensive. Hence, from the point of view of energy saving and to produce dark coatings the temperature was maintained between 25-30°C.

### Effect of anodising time

Anodising time affects considerably the colour of the coating. During the initial stages of anodising colour is of light tone and attains dark tones after prolonged anodising. Table II shows the effect of anodising time on the colour of the coating on B51S alloy at a voltage of 60 at 25 ± 2°C. The depth of colour depends on the treatment time.

Table II: Effect of anodising time on the colour obtained on B51S alloy using 5-sulphosalicylic acid 40 g/l, formic acid 40 ml/l, pyrogallol 10 g/l, 25 ± 2°C, 60 V a.c.

Time (mins)	Colour
15	Light grey
25	Chocolate
45	Brown
60	Black

### Influence of voltage and current density

There are essentially two techniques available for anodising, namely constant current density process and constant voltage process. In the former the current density is held constant and requires voltage rise of 0-120 V and needs vigorous cooling arrangement. The current density varies from 0.8 - 4.0 A/dm<sup>2</sup> depending on the temperature of the electrolyte and colour desired. In the latter method, the current density is held constant until some pre-arranged voltage between 50 and 80 V is reached, and thereafter, the voltage is held constant and the current allowed to decline naturally. The time of treatment is varied according to the colour desired. Table III shows the colour obtained on 2S aluminium at different voltages after 25 minutes of anodising. The thickness of the coating obtained at different voltages are also given in the Table. Coating thickness varies from 11-17 μm.

Table III: Effect of anodising voltage on the colour obtained in 2S alloy using 5-sulphosalicylic acid 40 g/l, formic acid 40 ml/l, pyrogallol 10 g/l, 25 ± 2°C, 25 minutes

Anodising voltage (V)	Colour	Coating thickness (μm)
50	Yellowish green	11
60	Brown	14
70	Chocolate	16
80	Dark brown	17

A simple source of a.c. at about 120 V is the minimum requirement. When the voltage is first applied, a relatively high current passes, which gradually falls as the insulating oxide film builds up. As the voltage is stepped up, further passage of current occurs for a short period until finally after the full voltage has been applied, the entire article is covered with an insulating oxide coat. Coverage takes place over the entire area. As the operation proceeds and the oxide coat builds up, the current becomes increasingly concentrated on the uncoated areas.

### Effect of aluminium alloy

In the early days of anodising, processors had great difficulty in obtaining a good transparent coating over the entire surface of the aluminium part. This was caused by certain alloying elements and impurities not being uniformly dispersed or combined. The alloying elements or constituents are affected during anodising in four ways: (a) dissolved (b) oxides are formed (c) unaffected and (d) combination of (a), (b) and (c). Al-Si and Al-Cu are difficult to colour by this electrolyte. However, normal extrusion alloys such as B51S can be easily treated in the electrolyte. Table IV shows the colour obtained on 3S alloy at different voltages with different addition agents. It is clearly evident from the Table that different tones are obtained with different additives.

Table IV: Colour obtained on 3S alloy using 5-sulphosalicylic acid 40 g/l, formic acid 40 g/l, 25 ± 2°C, 25 minutes with pyrogallol and metol as addition agents

Anodising voltage (V)	Colour
<i>Pyrogallol, 10 g/l</i>	
50	Purple
60	Chocolate
70	Reddish brown
80	Brownish black
<i>Metol, 10 g/l</i>	
50	Medium grey
60	Dark grey
70	Brownish black
80	Black

### Influence of agitation

Practically all of the electrical energy during anodising is converted to heat. This heat must be dissipated rapidly by refrigerating the electrolyte and using air agitation. Insufficient agitation, which leads to higher electrolyte temperatures, can cause soft coatings or catastrophic dissolution of the coating and basis metal often called burning. Burning is caused by local overheating. As soon as one small area becomes overheated, the electrolyte begins to dissolve the coating, which lowers its resistance causing the damaged area to draw excessive current. This, in turn, raises the temperature, accelerating burning. This whole process may take as little as few seconds to damage a part permanently. Burning can be recognised as a rapid rise in amperage. This situation is controlled by immediately decreasing the voltage.

### Materials of construction

The anodising tank lining for integral colouring will normally be PVC or similar plastic rather than the lead lining frequently used for sulphuric acid anodising. Lead causes the decomposition of the electrolyte which gives

problem in anodising. Cooling coil is made of stainless steel or titanium.

### Solution maintenance

During operation of the bath other impurities besides aluminium build up in the solution as various constituents of the alloys being anodised dissolve in it. Great care should be taken to avoid contamination of the bath with oil or grease. Particles of oil become strongly adsorbed at the anode surface, resulting in opaque spots in the films which are unsightly. In addition to impurities introduced into the bath during anodising, care must be taken to ensure that the chemicals used to make up the solution do not contain high levels of harmful impurities such as chloride. While additions may make good the loss, it is better that only a low substantially constant level of aluminium (< 8 g/l) is permitted to accumulate and remain in the electrolyte. This is achieved by partly replenishing the electrolyte.

### CONCLUSION

Integral colour anodising of aluminium is carried out using alternating current in an electrolyte containing,

5-Sulphosalicylic acid ..... 40 g/l  
Formic acid ..... 40 m/l  
Pyrogallol, pyrocatechol, p-aminophenol or metol ..... 5-10 g/l

at 25-30°C, for 25-60 minutes. Current density varies from 0.8 - 4.0 A/dm<sup>2</sup> and the operating voltage 50-80 V. Different bath voltages give different coloured coatings. Colours ranging from yellowish green, brown, reddish brown, grey, purple, chocolate, brownish black and black are obtained. The colour depends on the composition of the alloy and operating conditions. The method of operation is by the constant voltage process. Addition agents permit production of darker coatings at high voltages without the problem of spark discharge.

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