

1

3,759,801

ELECTROLYSIS BATH AND PROCESS FOR ELECTROLYTICALLY COLORING ANODIZED ALUMINUM

Jos Patrie, 3 Chemin des Marronniers, Grenoble, France, and Michel Legrand, "Le Villard," Coublevie, France
No Drawing, Filed Nov. 18, 1971, Ser. No. 200,225
Claims priority, application France, Nov. 26, 1970, 7042544

Int. Cl. C23f 7/00, 9/02

U.S. Cl. 204—35 N

7 Claims

ABSTRACT OF THE DISCLOSURE

An electrolysis bath for coloring previously anodized aluminum and alloys of aluminum by means of an alternating current electrolysis in an aqueous acid solution containing nickel sulphate in an amount within the range of 50 to 150 g./liter, ammonium sulphate and boric acid in an amount within the range of 45 to 60 g./liter, and at a pH within the range of 3.5 to 5.2.

This invention relates to the coloring of the layer of alumina on the surface of aluminum and its alloys.

It is known that the layer of alumina can be colored by subjecting the anodized article of aluminum or alloys of aluminum to electrolytic treatment with alternating current, using a counter-electrode of nickel, in an acid nickel salt bath. It is possible in this way to obtain bronze color finishes of the kind required for architectural purposes.

The production of dark color finishes requires prolonged electrolysis and involves certain difficulties due to the phenomenon known as "rupture" of the layer of alumina. This is reflected in brilliant spots in the area where the layer has deteriorated.

It was found that the results of electrolysis could be improved with certain arrangements and with certain surface ratios of the electrode, as described in application Ser. No. 742,000, filed July 2, 1968, now U.S. Pat. 3,622,471. The described process does not permit the use of current densities higher than 0.3 to 0.4 a./dm.², based on the aluminum article. In fact, even with an optimum arrangement of the electrodes, rupturing still occurs when these intensities are exceeded by any appreciable amount.

Electrolysis times of the order of 15 minutes are required to produce dark color finishes at low current densities. It is obvious that it would be advantageous from the standpoint of economics to be able to increase the current density and shorten the electrolysis time and thus increase the productivity of the cells, and it is an object of this invention to achieve the same.

It is an object of this invention to provide a method and means for coloring, especially in dark shades, by electrolysis of previously anodized aluminum articles without subjecting the articles to rupture and in reduced electrolysis time.

In accordance with the practice of this invention, the electrolysis is carried out in a bath of nickel salt and boric acid, using alternating current, with current densities markedly higher than those which have heretofore been considered possible.

To obtain this result it has been found that the composition of the electrolysis bath must be modified considerably. Whereas, heretofore, it has been thought that the chemical ingredients formulated into the composition of the bath had to be present in relatively low concentrations of the order of 25 g./liter of NiSO₄·7H₂O, 25 g./liter of H₃BO₃ and 15 g./liter of (NH₄)₂SO₄, it has been found, in direct contrast thereto, that it is advantageous markedly to increase the concentration of the bath and to

2

buffer the solution heavily with boric acid. In this manner, it becomes possible to make use of a current density from two to three times greater for electrolysis without rupturing the layer of alumina and with marked decrease in electrolysis time.

Measurements of potential were made during electrolysis in the immediate vicinity of the nickel electrode. Appreciable variations of as much as 1.5 volts were observed in instances where high current intensities were employed with electrolysis baths of conventional composition. It was found that rupturing occurs in the layer of alumina when such high variations in potential occur in the vicinity of the nickel electrode. By increasing the boric acid concentration of the bath, such variations in potential have been found to be either prevented or greatly reduced with elimination of the rupturing phenomena, except in the instances of very extended electrolysis.

In accordance with the practice of this invention, an electrolysis bath which enables the use of a current density within the range of 0.7 to 1.5 a./dm.² is formulated to contain NiSO₄·7H₂O in an amount within the range of 50 to 150 g./liter, ammonium sulphate in an amount within the range of 25 to 35 g./liter, optionally with a small excess of sulphuric acid or ammonia added to adjust the pH value, and boric acid in an amount within the range of 45 to 60 g./liter as buffering agent. The bath can be operated at a temperature range within 20° to 35° C. In the preferred practice, use is made of 100 g./liter of NiSO₄·7H₂O, 30 g./liter of ammonium sulphate and 50 g./liter of boric acid, with variations of the described ingredients in the amount of ±10%. By operating at a temperature within the range of 25 to 35° C., with a current density of 0.75 to 1.5 a./dm.², it is possible to obtain a deep bronze color within a period of approximately 5 minutes and a substantially black color finish over a period of from 10 to 20 minutes, depending upon the current density and with the pH value and surface ratio of electrolysis also having a slight bearing upon the results. If, for example, the surface ratio of the Al/Ni electrodes is 2, the pH value should not exceed 4.5, while with a surface ratio of 8, good results can be obtained in a pH range of 3.5 to 5.2.

EXAMPLES

The object of the following examples is to demonstrate the influence which the boric acid concentration has upon the rupturing of the layer of alumina in nickel sulphate baths, during an electrolysis operation carried out with 50 c./s. alternating current, a constant current density of 0.8 a./dm.², for a period of 6 minutes, which is sufficient to form a dark bronze layer.

The metal used was a plate of commercial 99.5% pure aluminum containing the usual impurities, mainly silicon and iron. After the conventional treatments of degreasing and scouring, the metal is anodized in a sulphuric acid bath, containing 20% by weight of H₂SO₄, over a period of 30 minutes, at a temperature of 20° C., and at a current density of 1.5 a./dm.² (D.C. voltage). The layer of alumina has a thickness of 12 microns.

The coloring bath had the following composition:

	G./liter
NiSO ₄ ·7H ₂ O -----	100
(NH ₄) ₂ SO ₄ -----	30
H ₃ BO ₃ -----	125 or 50

¹ Depending on the tests.

The pH value of the solution is adjusted to the required value for each series of tests by addition of a small quantity of a dilute solution of H₂SO₄ or NH₃. The temperature of the bath was maintained at 30° C. during electrolysis.

The cell used for the tests was a Hull cell. It is in the form of a parallelepiped, the base of which is a rectangular trapezium. The working conditions are hardly favorable to the production of uniform color finishes because the surfaces of the electrode are not parallel but instead form a dihedral angle of 50°.

The nickel counter-electrode is placed on the vertical wall, perpendicular to the parallel sides of the trapezium, while the anodized aluminum plate is placed on the surface opposite the counter-electrode. By using flat electrodes with as large a surface as possible, the Al/Ni ratio is 2. In those tests in which the Al/Ni surface ratios differ from 2, plates of nickel or aluminum with calculated dimensions were employed.

By examining the aluminum plate upon completion of the operation, it is possible readily to detect the faults attributable to rupturing, which appear in the form of brilliant spots in those areas where the base metal has been exposed.

(1) The following Table I relates to the tests carried out at various pH values with various Al/Ni surface ratios of the electrodes, in a bath containing 25 g./l. of boric acid. In other words, these tests were not carried out in accordance with the practice of this invention.

TABLE I

pH.....	5.2	5.8	4.5
Al/Ni:			
2.....	Numerous ruptures..... Irregular color finish..... Beginning 10 ^v , end 17 ^v	Incipient ruptures..... Deep color finish..... Beginning 10 ^v , end 16 ^v	Numerous ruptures. Deep color finish. Beginning 11 ^v , end 17 ^v .
8.....	Numerous ruptures..... Deep color finish..... Beginning 10 ^v , end 17 ^v	Incipient ruptures..... Deep color finish..... Beginning 10 ^v , end 10 ^v	
16.....	Numerous ruptures..... Deep color finish..... Beginning 10 ^v , end 16 ^v		Numerous ruptures. Deep color finish. Beginning 10 ^v , end 17 ^v .

It will be seen that, irrespective of the surface ratio of the electrodes, it is not possible, with a bath containing 25 g./l. boric acid, to obtain a good color finish with a current density of 0.8 a./dm.². At a pH value of 4.8, the results are the least unfavorable, although nevertheless incipient rupturing is observed and the voltage at the terminals increases rapidly at constant current density.

(2) Comparable tests were carried out, but this time with a bath containing 50 g./liter of boric acid, with the other conditions being the same as set forth in paragraph (1) above. The results obtained are set forth in the following Table II.

TABLE II

pH.....	5.2	4.5
Al/Ni:		
1.....		No rupturing. Very deep color finish. Beginning 11 ^v .
2.....	Incipient rupturing..... Average color..... Beginning 11 ^v , end 18 ^v	No rupturing. Very deep color finish. Beginning 10 ^v , end 14 ^v .
8.....	No rupturing..... Average color..... Beginning 10 ^v , end 16 ^v	No rupturing. Very deep color finish. Beginning 10 ^v , end 14 ^v .
16.....	No rupturing..... Very deep color finish..... Beginning 10 ^v , end 14 ^v	No rupturing. Very deep color finish. Beginning 10 ^v , end 14 ^v .

It can be seen, by comparing the data of Table II with that of Table I, that the increase in the boric acid content of the bath has completely changed the results. Even at a pH value of 5.2, which is abnormally high, it was possible to obtain excellent results where the surface ratio of the electrodes is sufficiently high. It is, in effect, necessary to have a current density that is fairly high in relation to the nickel electrode in order to insure uniform corrosion. By contrast, at a pH value of 4.5, excellent results are obtained with all of the surface ratios of the electrodes. The voltage undergoes hardly any increase during electrolysis.

The first test identified in Table II was carried out with a plate of anodized aluminum of reduced surface. After 6 minutes' electrolysis, the voltage had increased to 14 volts. The operation was then continued until signs of rupturing appeared in the layer of alumina. This occurred only after 40 minutes at a final voltage of 17 volts. The color finish was completely black by this time.

These tests show that, with a bath formulated in accordance with the practice of this invention, it is possible, at a suitable pH value, rapidly to obtain a dark or very dark bronze color finish by carrying out electrolysis at a high current density. The surface ratio of the electrodes is relatively unimportant when use is made of a bath having a pH of 4.5, containing 50 g./liter of boric acid.

(3) In another series of tests, using the same bath composition as in Example 2, an electrode surface ratio of 8 and a current density of 0.8 a./dm.², the pH value was varied from 3.5 to 5.2. In every instance, a very dark color finish, free of any signs of rupturing, was obtained in 6 minutes.

(4) In the same bath as in Example 3, containing 50 g./liter of boric acid and a pH value of 4.5, a uniform, substantially black color finish was obtained by continuing electrolysis at 0.8 a./dm.² for 15 minutes and by using a

current density of 1.5 a./dm.² for 8 minutes. There were no indications of rupturing, even with a surface ratio of Al/Ni electrodes of only 2.

These examples show that, by using nickel salt baths containing approximately 100 g./liter NiSO₄·7H₂O and approximately 50 g./liter boric acid, it is possible to use current densities much higher than those heretofore found to be acceptable. It is possible in this way to obtain dark, very dark or even practically black "bronze" color over a period of time, much shorter than that heretofore required.

By using the Hull cell, of the type employed in the examples, the tests were voluntarily carried out under conditions most unfavorable to the production of a uniform color layer. The same bath composition was then used in industrial cells having a capacity of several cubic meters, with electrodes arranged parallel to one another. The results obtained fully confirmed the ability very quickly to produce dark color finishes, free from rupturing, using current densities of the order of 0.7 to 1.3 amperes per dm.², on aluminum, or aluminum alloys having an alumina layer formed by previous anodization.

It will be understood that changes may be made in the details of formulation and operation without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. An electrolysis bath for coloring previously anodized aluminum and its alloys by means of alternating current electrolysis in an aqueous acid solution having a pH within the range of 3.5 to 5.2 and containing nickel sulphate, ammonium sulphate and boric acid in which the nickel sulphate (NiSO₄·7H₂O) is present in an amount within the range of 50 to 150 g./liter and the boric acid is present in an amount within the range of 45 to 60 g./liter.

2. An electrolysis bath as claimed in claim 1 in which the NiSO₄·7H₂O is present in an amount within the range of 90 to 100 g./liter and H₃BO₃ is present in an amount within the range of 45 to 55 g./liter.

5

3. An electrolysis bath as claimed in claim 2 in which the bath has a pH within the range of 4.2 to 4.8.

4. A process for coloring articles of aluminum and aluminum alloys having an alumina surface by subjecting the articles to alternating current electrolysis with a nickel counter-electrode in an electrolysis bath having the composition claimed in claim 1 at a temperature within the range of 20 to 35° C. and a current density within the range of 0.7 to 1.5 a./dm.².

5. A process as claimed in claim 4 in which the electrolysis for coloring the article is carried out for a period of time within the range of 5 to 20 minutes.

6. A process as claimed in claim 4 in which the electrolysis bath is adjusted to a pH within the range of 4.2 to 4.8.

6

7. Articles of aluminum or alloys of aluminum the surfaces of which are colored by the process claimed in claim 4.

References Cited

FOREIGN PATENTS

2,052,132 4/1971 France ----- 204—35 N

JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

U.S. Cl. X.R.

204—58; 106—1

15