

March 19, 1974

W. P. KAMPERT

3,798,137

DIRECT CURRENT PIGMENTING OF ANODIZED ALUMINUM

Filed March 22, 1972

2 Sheets-Sheet 1

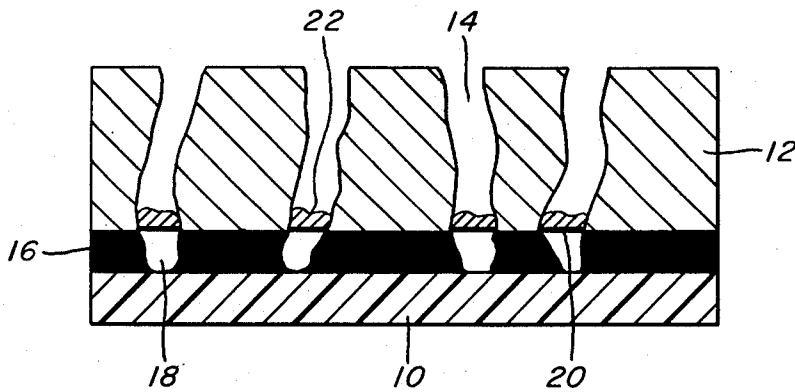


FIG. 1

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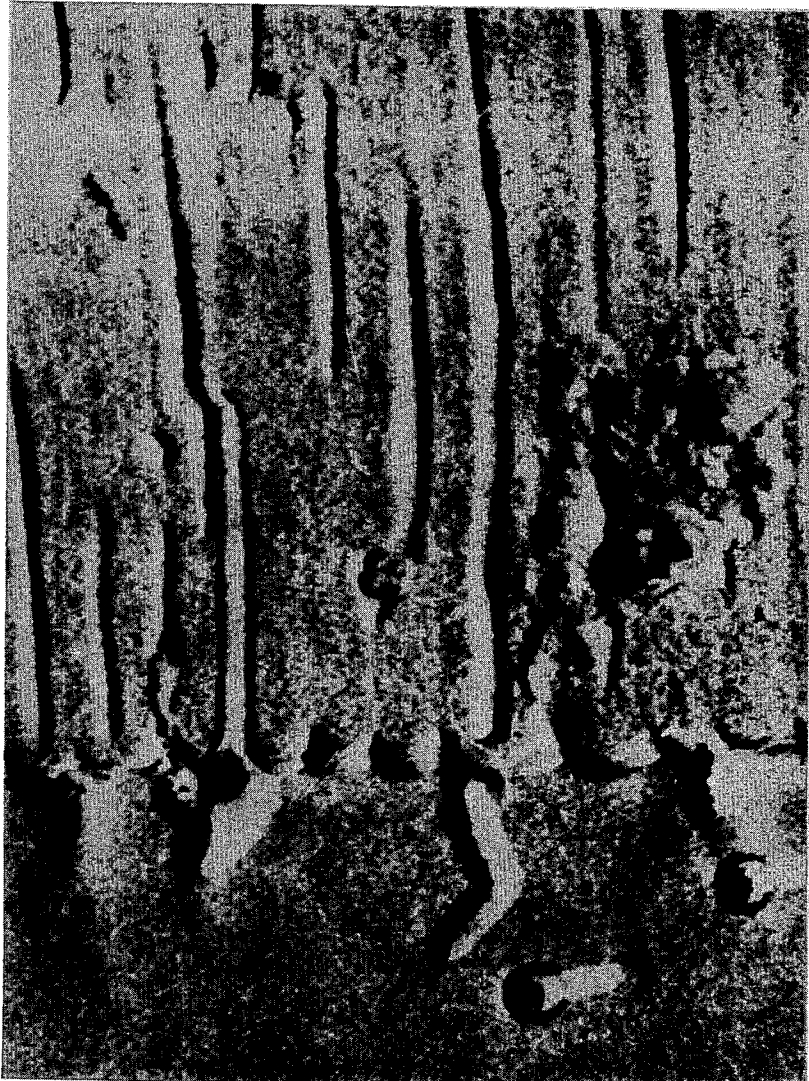


FIG. 2

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DIRECT CURRENT PIGMENTING OF ANODIZED ALUMINUM

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7 Claims

ABSTRACT OF THE DISCLOSURE

Direct current electrolytic coloring of anodized aluminum with As, Sb, Bi, Cu, Ag, Cd, Sn, Se, Te and Tl.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to coloring of aluminum. More particularly, it relates to employing direct current for cathodic deposition of metallic coloring pigments into anodized aluminum coatings from an acidic electrolyte containing cations of As, Sb, Bi, Cu, Ag, Cd, Sn, Se, Te or Tl.

By aluminum I mean aluminum containing minor amounts of impurities or incidental elements and aluminum base alloys containing at least about 80% by weight aluminum.

Description of the prior art

Colored oxide coatings on aluminum can be produced by formation of a porous oxide coating thereon, for example, by D.C. or A.C. anodizing, followed by A.C. deposition of pigments from acid electrolytes. However, numerous disadvantages are inherent in the use of alternating current for deposition of pigments. For example, since most shops conventionally employ direct current power, an A.C. source of power and related control equipment must be acquired if A.C. coloring is to be employed. Furthermore, use of A.C. requires adjustments in the number and placing of counterelectrodes to maintain the desired cathodic and anodic current density distribution. An additional disadvantage of use of A.C. in coloring porous oxide coatings on aluminum is the diminishing of the adhesion of the oxide coating to the basis metal because of coating disruption near the metal/oxide film interface. Moreover, because most A.C. pigment deposition methods require dilute acid solutions containing dissolved metal ion, the conductivity and throwing power of these electrolytes are quite low. This means that the capability of methods employing A.C. to plate pigmenting or coloring ions into recessed areas is often unsatisfactory.

SUMMARY OF THE INVENTION

After extended investigation, I have found that the foregoing problems may be solved by employing direct current to plate As, Sb, Bi, Cu, Ag, Cd, Sn, Se, Te and Tl into anodic oxide coatings. The anodic oxide coatings into which these metallic coloring pigments are plated are produced by known methods of anodizing aluminum. They incorporate a relatively thin, nonporous barrier oxide layer adjacent to the aluminum basis metal, which is overlaid with a relatively porous layer of the oxide. Any conventional electrolyte known to produce such an anodic oxide coating by employing known anodizing techniques may be used. The thickness of the barrier layer of the

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anodic oxide coating is substantially proportional to the formation voltage. I have found that sites suitable for electrodeposition of metallic pigments by direct current may be formed in the barrier layer when the basis metal contains as a modifying constituent an additional element or a complex of two or more additional elements. The modifying constituent must be of sufficient size to penetrate the barrier layer, which is at least 50 angstroms in thickness, and be present in an amount which, when dissolved or left in the oxide coating during production thereof by anodizing, forms sufficient sites for deposition thereof of the coloring cations. By "of sufficient size to penetrate the barrier layer," I mean of a length at least as great as the thickness of the barrier layer. This enables current to be conducted from the acid electrolyte through the porous layer and barrier layer of the anodic oxide coating to the basis metal as cathode when a modifying constituent during anodizing has extended through the barrier layer or has made a path therethrough, whether or not partially or completely dissolved. At least 30 sites per square micron of basis metal surface are generally sufficient for production of the desired color.

Representative of modifying constituents which enable formation of the required sites and electrolytic deposition thereof of the aforementioned cationic coloring pigments are magnesium silicide (Mg_2Si), magnesium-zinc ($MgZn_2$), and one or more of chromium, manganese, copper and cobalt.

Plating metal cations according to the invention permits use of strong acid solutions as the vehicle to plate the color-producing cation into the porous oxide coating. Other advantages include (1) use of conventional already-installed or readily obtainable anodizing equipment, (2) increased "throwing" power of the plating solution, (3) use of voltages as low as 2 volts, (4) avoidance of loss of adherence of the oxide coating, and (5) elimination of the necessity for balancing the number and placement of counterelectrodes relative to the work load when it is changed in size and geometry.

The aluminum to be treated according to the invention may be cleaned or etched in any conventional manner prior to anodizing. The anodizing may be by D.C. or A.C. Conventional anodizing electrolytes such as sulfuric acid or a mixture of sulfophthalic or sulfosalicylic acid with sulfuric acid may be used. The anodic coating on the anodized aluminum treated according to the invention may range, for example, from 0.3 mil to 10 mils in thickness, the thickness being controllable by well-known techniques of varying time, temperature and current.

Preferred electrolytic cationic coloring conditions according to the invention include a temperature of from about 15 to about 30° C., a current of from about 1 to about 24 a.s.f. and a time of from about 2 to about 30 minutes. The anode may be made of conventional materials known for use in anodes, for example, a metal such as stainless steel or a form of carbon such as graphite.

Representative colors which may be formed according to the D.C. pigmenting process of the invention are as follows: for arsenic, yellow gold; for antimony, gray bronze; for bismuth, bronze; for copper, red bronze; for silver, yellow brown; for cadmium, bronze; for tin, gray bronze; for selenium, yellow gold; for tellurium, pewter gray; and for thallium, bronze.

Applying less than 1 a.s.f. in the coloring procedure of the invention unduly prolongs the time required for de-

velopment of the desired color. Use of a current density of less than 1 a.s.f. also exposes the specimen undergoing treatment to an unnecessarily long exposure to the dissolving effect of the electrolyte. This may cause a "softer" or less dense coating. Use of cathodic current densities greater than 24 a.s.f. tends to cause spalling or blistering of the anodic coating due to the excessive amount of hydrogen gas evolved. The preferred operating current density range is from about 1 to about 4 a.s.f.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention, reference will now be made to the drawings, in which:

FIG. 1 is an illustrative schematic representation of one concept of what aluminum having a porous oxide coating thereon colored according to the invention looks like. Basis metal aluminum 10 has an anodic coating thereon made up of an external porous oxide layer 12 with pores 14 therein and an internal barrier layer 16 with modifying constituents 18 penetrating therethrough and forming sites 20 at which is deposited cationic coloring pigment 22.

FIG. 2 is a photocopy of a micrograph section (120,000 $\times$) showing coloring copper pigment deposited on sites formed by Mg_2Si modifying constituents penetrating the barrier layer of a porous oxide coating on an aluminum/magnesium-silicide alloy basis metal. The coloring copper pigment was deposited into the anodic coating of the aluminum alloy by passing a direct current of 2 a.s.f. through a 15% by weight sulfuric acid solution at about 21° C. for about 15 minutes at a voltage of 1.8.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are illustrative of the invention.

The gelatin employed in several of the examples is to aid in minimizing buildup of superficial metallic deposits on edges or corners of components being colored according to the invention. However, use of gelatin in the coloring or pigmenting bath employed according to the invention is not essential in practicing the invention.

EXAMPLE 1

An extruded aluminum base alloy piece approximately 2½" x 8" in size, and containing 0.48% Si, 0.26% Fe, 0.05% Cu, 0.01% Mn, 0.53% Mg, 0.02% Zn and 0.04% Ti, was artificially aged for 1 to 2 hours at 232-246° C. It was degreased with acetone prior to deoxidizing in an alkaline solution at 65.5° C. for 5 minutes, etching in 5% NaOH solution at 54.4° C. for 5 minutes and desmutting in 40 wt. percent HNO_3 solution at room temperature (about 20° C.). The sample was then anodized with direct current for 30 minutes in a 16% by weight H_2SO_4 electrolyte containing 1 g./l. Bi_2O_3 and 10 g./l. gelatin. The temperature of the electrolyte was maintained at 24° C., the current density was held at 24 a.s.f., and the voltage amounted to approximately 16 volts. A stainless steel plate served as the cathode in the cell. A uniform, translucent anodic oxide coating of about 1 mil thickness resulted. The electrical power source was switched off and, without the necessity of removing the specimen from the electrolyte, the current leads to the anodizing vessel were reversed so that the anodically coated specimen became the cathode and the stainless steel plate became the anode. The electric power was switched on a direct current potential of 2.6 volts was impressed across the cell so as to produce a cathode current density of 8 a.s.f. After 5 minutes of this treatment, the oxide coating was found to be of a uniformly colored medium bronze shade. The colored specimen was then removed from the electrolyte, rinsed in water, and sealed for 25 minutes in boiling deionized water.

EXAMPLE 2

This example illustrates how two separate vessels and electrolytes may be used in the process of the invention,

the first for forming the anodic coating and the second for coloring it.

A specimen of the alloy of Example 1 was prepared for anodizing in the same manner as described in Example 1. The specimen was suspended in a tank containing 16 wt. percent H_2SO_4 at 21° C. and anodized for 30 minutes with a direct current density of 24 a.s.f. This treatment resulted in a translucent oxide coating of about 1 mil thickness. The anodically coated specimen was then transferred to a second tank where it was made the cathode in a 15 wt. percent H_2SO_4 electrolyte containing 1 g./l. Bi_2O_3 and 10 g./l. gelatin. A stainless steel plate served as the anode, and a cathodic current density of 8 a.s.f. was passed for 5 minutes by maintaining a D.C. potential of 2.6 volts across the cell. This treatment caused the oxide coating to become medium bronze in color, similar in shade to the specimen colored in Example 1. The specimen was then rinsed in water and sealed as in Example 1.

EXAMPLE 3

Various shades of metallic bronze were developed on an extruded anodized alloy such as that of Example 1 by using as coloring electrolyte 16 wt. percent sulfuric acid containing 1 g./l. As_2O_3 .

A rich yellow-gold color resulted from a 20-minute treatment at 8 a.s.f. and 21° C.

EXAMPLE 4

An electrolyte composed of 16 wt. percent sulfuric acid and 1 g./l. $SnSO_4$ produced gray-bronze colors on the same anodized extruded alloy as that of Example 1 treated similarly except for the different electrolyte used.

EXAMPLE 5

Decorative shades of red were produced on the anodized extruded alloy of Example 1 when processed according to the invention in a 16 wt. percent H_2SO_4 electrolyte containing 2 g./l. $CuSO_4$ and 2 g./l. gelatin. At 26.7° C., this electrolyte produced a copper color on a specimen anodized in a H_2SO_4 electrolyte treated as cathode for 5 minutes at 8 a.s.f. while employing a graphitic carbon anode. Deeper shades of red-bronze (maroons) resulted from longer times of treatment in this bath. A rich mahogany color was obtained when the alloy of Example 1 was replaced by one containing more Cu and Cr, viz., 0.50% Si, 0.26% Fe, 0.55% Cu, 0.52% Mg, 0.23% Cr, 0.02% Zn, 0.03% Ti.

EXAMPLE 6

A H_2SO_4 electrolytic anodic oxide coating on the alloy of Example 1 developed a medium bronze color when treated cathodically for 15 minutes at 8 a.s.f. in a 16 wt. percent sulfuric acid electrolyte containing 1 g./l. $CdSO_4$.

EXAMPLE 7

A H_2SO_4 electrolytic anodic oxide coating on the alloy of Example 1 developed a "pewter gray" color when treated cathodically for 15 minutes at 2 a.s.f. in a 16 wt. percent sulfuric acid electrolyte containing 1 g./l. TeO and 1 g./l. gelatin.

EXAMPLE 8

This example illustrates the need for use of an acid electrolyte in the cathodic coloring step of the invention.

An extrusion alloy of the composition of the alloy in Example 1 previously anodized in 16 wt. percent H_2SO_4 at 21.1° C. for 50 minutes at 12 a.s.f. was used as cathode and treated in each of the electrolytes shown in the following table (Table I), for 20 minutes at 28° C. and at a direct current of 8 a.s.f. The resulting colors or lack of color are shown in the table. The electrolyte in each of the samples in the following table contained 1 g./l. gelatin.

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TABLE I

Electrolyte:	Color
(1) 100 g./l. HNO ₃ ; 1 g./l. Bi ₂ O ₃ .	Med. bronze.
(2) 100 g./l. HCl; 1 g./l. Bi ₂ O ₃ .	Dark bronze.
(3) 100 g./l. NaCl; 1 g./l. Bi ₂ O ₃ .	No color.
(4) 100 g./l. NaCl; 1 g./l. CuSO ₄ .	Do.
(5) 100 g./l. K ₂ SO ₄ ; 1 g./l. CuSO ₄ .	Do.
(6) 100 g./l. NH ₄ NO ₃ ; 1 g./l. Cu(OH) ₂ .	Do.
(7) 100 g./l. (NH ₄) ₃ PO ₄ ; 1 g./l. Bi ₂ O ₃ .	Do.

EXAMPLE 9

Table II, which follows, shows the colors produced according to the invention by using varying amounts of Cu, Cr, Co and Mn as the modifying constituent in the anodized alloy. Specimens of each alloy were anodized in 16 wt. percent H₂SO₄ with a direct current density of 12 a.s.f., for 50 minutes at 21° C. and a voltage ranging from 10 to 18. Color of the anodized specimens prior to D.C. cathodic treatment according to the invention is shown in each instance in Table II. The cathodizing electrolyte was 16 wt. percent H₂SO₄ containing 1 g./l. CuSO₄·5H₂O or 1 g./l. Bi₂O₃, as indicated, and 1 g./l. gelatin. Cathodizing conditions included a current density of 8 a.s.f. for 20 minutes at 26.7° C.

TABLE II

Modifying alloy constituent	Color of anodic coating (15% H ₂ SO ₄)	Color from Bi	Color from Cu
.14% Cu.....	Colorless.....	Colorless.....	Colorless.
.98% Cu.....	Med. gold.....	Black.....	Dark bronze.
3.85% Cu.....	Colorless.....	Dark bronze.....	Med. gray bronze.
.19% Cr.....	do.....	Lt. bronze.....	Lt.-pink bronze.
.36% Cr.....	Med. gold.....	Med. gold.....	Med. gold.
.83% Co.....	Lt. gray.....	Dark gray.....	Med. pink gray.
2.0% Mn.....	Lt.-med. gray.....	Med.-dark gray.....	Med. pink.

EXAMPLE 10

Table III, which follows, compares for the two sheet alloys and one extrusion alloy shown the colors produced by employing D.C. according to the invention with those produced by employing A.C. according to the prior art. The concentration of the sulfuric acid electrolyte used was varied at levels at 5, 10, 20, 70 and 150 g./l. as indicated.

TABLE III

Coloring electrolytes	Potential	Color description		
		Extrusion alloy ¹	Sheet alloy A ²	Sheet alloy B ³
5 g./l. H ₂ SO ₄ , 1 g./l. CuSO ₄ ·5H ₂ O—Conductance 0.027 mhos/cm.	AC	No color.....	Very slight tan cast.....	No color.
	DC	Red bronze.....	No color.....	Very slight gray tan.
5 g./l. H ₂ SO ₄ , 1 g./l. CuSO ₄ ·5H ₂ O, 1 g./l. gelatin....	AC	Very slight gray tan.....		
	DC	Red bronze.....		
10 g./l. H ₂ SO ₄ , 1 g./l. CuSO ₄ ·5H ₂ O, 1 g./l. gelatin—Conductance 0.049 mhos/cm.	AC	Very slight gray tan.....	Very slight gray tan.....	No color.
	DC	Red bronze.....	No color.....	Slight gray tan.
20 g./l. H ₂ SO ₄ , 1 g./l. CuSO ₄ ·5H ₂ O, 1 g./l. gelatin—Conductance 0.09 mhos/cm.	AC	Very slight gray tan.....	Very slight tan.....	Slight tan.
	DC	Red bronze.....	No color.....	Slight pink tan.
70 g./l. H ₂ SO ₄ , 1 g./l. CuSO ₄ ·5H ₂ O, 1 g./l. gelatin—Conductance 0.27 mhos/cm.	AC	Dark gold.....	Medium gold.....	Light antique gold.
	DC	Red bronze.....	No color.....	Slight gray tan.
150 g./l. H ₂ SO ₄ , 1 g./l. CuSO ₄ ·5H ₂ O, 1 g./l. gelatin—Conductance 0.48 mhos/cm.	AC	Medium to dark gold.....	Light to medium gold.....	Light to medium gold.
	DC	Red bronze.....	No color.....	Slight pink tan.

¹ Same composition as alloy of Example 1.

² 0.07% Si, 0.55% Fe, 0.12% Cu, 0.01% Mn, 0.01% Zn, 0.02% Zn.

³ 0.2% Si, 0.6% Fe, 0.1% Cu, 1.1% Mn.

EXAMPLE 11

Two anodized aluminum base alloys containing Zn and Mg were treated according to the invention, Alloy A having 0.25% Si, 0.40% Fe, 0.03% Cu, 0.5–0.9% Mg, 3.6–4.4% Zn and 0.10% Ti and Alloy B having 3.80% Zn and 1.00% Mg. The modifying constituent for both alloys was the intermetallic compound MgZn₂. Treatment conditions are shown in the following Table IV.

TABLE IV

Porous oxide coating:	Coloring according to the invention
15% H ₂ SO ₄ -----	15% H ₂ SO ₄ +1 g./l. CuSO ₄ +1 g./l. gelatin.
21.1° C. -----	26.7° C.
12 a.s.f. -----	2 a.s.f.
50 min. -----	20 min.

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Prior to anodizing both alloys were solution heat treated at 480° C. for 1 hour. One sample of each alloy was artificially aged for 2 hours at 240° C. and the other was not artificially aged. Photomicrographs were made of the aged and unaged samples of each alloy. For Alloy A, in the photomicrograph of the artificially aged sample were seen constituents that were not dissolved when the sample was solution heat treated. The sample not artificially aged developed good color although not as much as the aged one, which developed an attractive reddish black color.

Similar results were obtained with Alloy B except that in the unaged sample there were no constituents of any kind noted, and consequently this sample did not color.

In both alloys the constituents precipitated were compounds of Mg-Zn, and in both cases artificial aging increased the amount of sites formed by modifying constituents and, in turn, the amount of color development.

It thus appears that if there is a sufficient number of sites created by modifying constituents of the required barrier layer penetrating size explained hereinabove, no matter how produced, good color can be obtained according to the process of the invention.

EXAMPLE 12

A single high-purity aluminum base alloy in sheet form containing 1% Mg₂Si was anodized in two different electrolytes. The first was a 15% sulfuric acid electrolyte and the second a 9.7% sulfophthalic/0.5% H₂SO₄ electrolyte. The sample anodized in the H₂SO₄ electrolyte was treated for 50 minutes at 12 a.s.f. and 21° C. and the sample anodized in the sulfophthalic-H₂SO₄ acid electrolyte was anodized for 20 minutes at 24 a.s.f. and 24° C. Prior to anodization, both samples were solution heat treated for 2 hours at 549° C. Each of the two samples was then divided into three parts, one of which was aged for 17 hours at 149° C., another for 3 days at 204.4° C. and the third for 3 hours at 315.5° C. The six parts were then employed as cathodes using direct current in a 15% H₂SO₄ electrolyte containing 1 g./l. each of CuSO₄ and gelatin. The three parts anodized in H₂SO₄ were treated for 15 minutes at 2 a.s.f. and 26.7° C. and the three anodized in sulfophthalic-H₂SO₄ for 20 minutes at 2 a.s.f. and

26.7° C. The parts anodized in the sulfophthalic-H₂SO₄ had bronze-colored oxide coatings. Although only a slight color was observed on the sample aged for 17 hours at 149° C. and anodized in H₂SO₄, a substantially uniform red was obtained for the sample aged for 3 days at 204.4° C. The third part of the same H₂SO₄-anodized sample aged 3 hours at 315.5° C. also showed little color, possibly because some of the smaller Mg₂Si modifying constituents were dissolved and re-precipitated on larger ones, thus effectively reducing their number. The sulfophthalic/H₂SO₄-anodized parts aged for 17 hours at 149° C. and for 3 days at 204.4° C. showed little, if any, change in color as a result of the cathodizing treatment. The sulfophthalic/H₂SO₄-anodized parts aged for 3 hours at 315.5° C. developed a dark, almost black, color after the cathodizing treatment. FIG. 2 is a copy of a photomicrograph of a section of this specimen (120,000X).

From counts made for specimens of this example of number of sites required for most acceptable color development, it was found that 70 particles per square micron of basis metal surface resulted in excellent color development, 20 sites per square micron resulted in generally unacceptable color development and 30 sites per square micron resulted in reasonably acceptable color development.

While the invention has been described in terms of preferred embodiments, the claims appended hereto are intended to encompass all embodiments which fall within the spirit of the invention.

Having thus described my invention and certain embodiments thereof, I claim:

1. A process for coloring aluminum having an anodic oxide coating thereon which comprises flowing a direct current having a density ranging from about 1 to about 24 a.s.f. from an anode in respective order through:

- (1) an acid electrolyte at a temperature of from about 15° C. to about 30° C. and containing a color-forming cation selected from the group consisting of As, Sb, Bi, Cu, Ag, Cd, Sn, Se, Te, and Tl,
 - (2) a porous external portion of the anodic oxide coating on aluminum basis metal, and
 - (3) sites at a barrier layer at least 50 angstroms thick adjacent the basis metal, the density of said sites being at least 30 per square micron of the surface of said basis metal,
- to the basis metal as cathode, said basis metal containing modifying constituents selected from the group consisting of Mg₂Si, MgZn₂, Cu-Cr, Cr, Co, Cu and Mn of sufficient size and number to penetrate said barrier layer,

thereby depositing at said sites in said anodic oxide coating a sufficient amount of said cation to form a visible color.

2. The process of claim 1 wherein the cation is associated with a chloride, nitrate, sulfate or oxide anion.

3. The process of claim 1 wherein the direct current is flowed for from about 2 to about 30 minutes.

4. The process of claim 1 wherein the direct current is flowed at from about 1 to about 4 a.s.f.

5. The process of claim 1 wherein the thickness of the anodic oxide coating is from about 0.3 mil to about 10 mils.

6. The process of claim 1 wherein said anodic oxide coating is colorless.

7. The process of claim 1 wherein said anodic oxide coating is colorless.

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JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,798,137 Dated March 19, 1974

Inventor(s) William P. Kampert

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 38	After "invention." change "However" to --However--.
Col. 5, line 9	After "g./l." change ")NH ₄)" to --(NH ₄)--.
Table III, line 7	After "10 g./l." change "H ₂ OS ₄ " to --H ₂ SO ₄ --.
Claim 7, line 2	After "is" change "colorless" to --colored--.

Signed and sealed this 30th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents