

[54] **ARTICLE WITH A MULTICOLORED SURFACE DECORATION THEREON PRODUCED BY LIGHT INTERFERENCE EFFECTS**

[76] Inventors: Nadezhda Vasilievna Rjumshina, Sovetskaya, 13, Solntsevo; Gennady Fedorovich Vasiliev, K-482, Korpus 331 kv. 93; Georgy Markovich Vozlinsky, K-482 Korpus 447, kv. 30, both of Moscow, all of U.S.S.R.

[22] Filed: July 19, 1971

[21] Appl. No.: 163,684

Related U.S. Application Data

[62] Division of Ser. No. 702,877, Feb. 5, 1968, Pat. No. 3,619,385.

[52] U.S. Cl. 204/18 R, 204/15

[51] Int. Cl. C23b 5/48, B44c 1/04

[58] Field of Search 204/18, 32, 15, 35 N, 204/38 A, 37, 56; 156/18

[56] References Cited

UNITED STATES PATENTS

705,456 7/1902 Sinclair 204/18 R
2,934,480 4/1960 Slomin 204/56 R

3,075,896 1/1963 McGraw et al. 204/56 R
2,059,053 10/1936 Stareck 204/18 R

FOREIGN PATENTS OR APPLICATIONS

3,912,761 1964 Japan 204/18 R

Primary Examiner—John H. Mack

Assistant Examiner—T. Tufariello

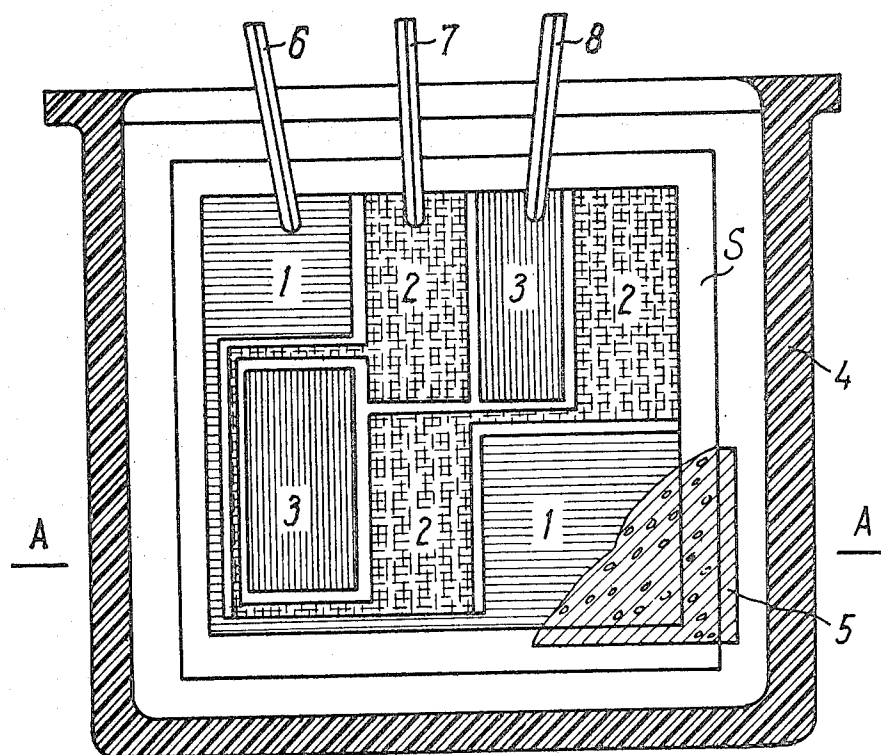
Attorney—Eric H. Waters et al.

[57]

ABSTRACT

A polychromatic image is formed on the surface of an article by depositing on a solid dielectric layer a thin film of a unilaterally-conducting metal or alloy thereof to a thickness of at least 500 Å, followed by dividing the film into separate areas in conformity with the shape of the picture to be reproduced, the areas being electrically insulated from one another. Thereafter the areas are subjected to selective anodic oxidation at a constant current density of less than 10 mA/cm² and at working voltages which vary from one area to another in a range of 5 to 250 volts to produce transparent anodic oxide films on the areas of thicknesses between 100 to 6,000 Å, to impart different coloration to the areas by light interference phenomena.

4 Claims, 4 Drawing Figures



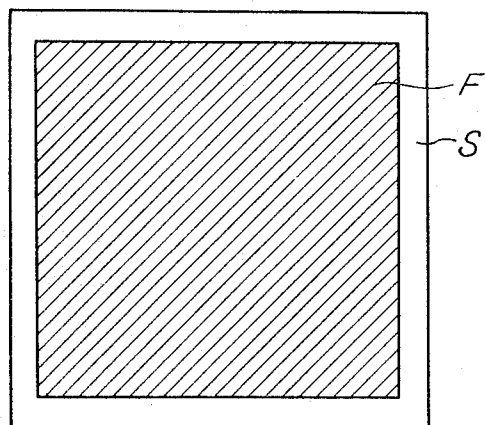


FIG. 1

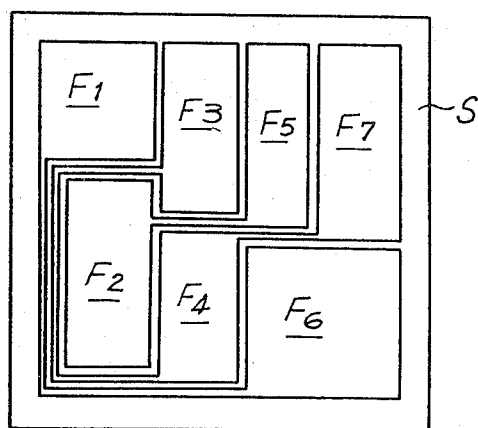


FIG. 2

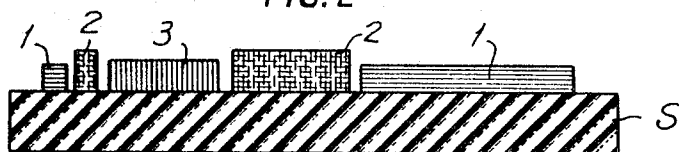


FIG. 4

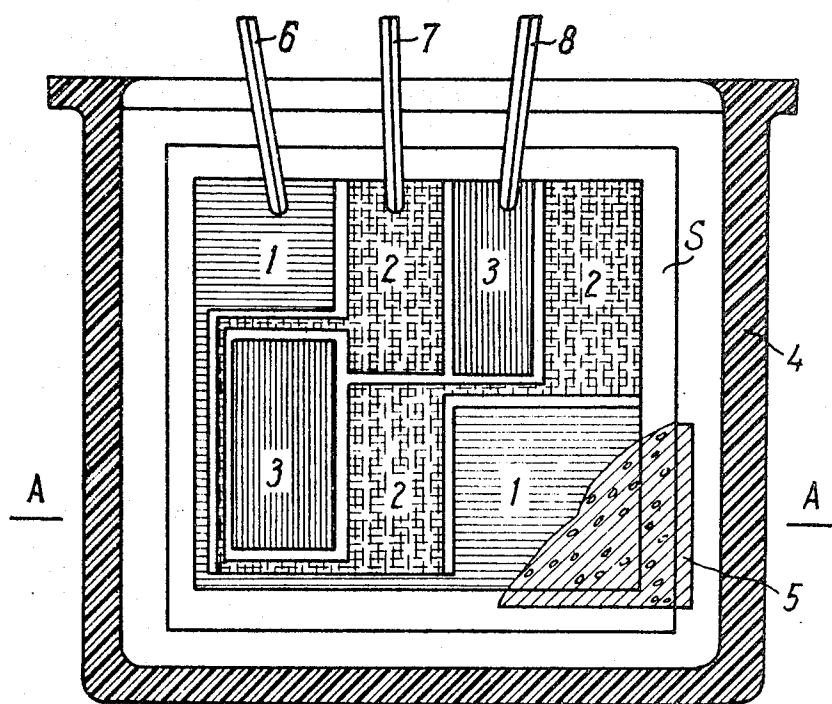


FIG. 3

ARTICLE WITH A MULTICOLORED SURFACE DECORATION THEREON PRODUCED BY LIGHT INTERFERENCE EFFECTS

CROSS RELATED APPLICATION

This application is a division of our earlier application Ser. No. 702,877 filed Feb. 5, 1968, now U.S. Pat. 3,619,385.

FIELD OF INVENTION

This invention relates to decorative and protective surface finishing and, particularly, to articles having multicolor decorations thereon.

BACKGROUND

The invention may find extensive application in diverse industrial fields, such as machine building, optics, watch- and clock-making, jewelry as so forth.

The production of polychromatic film coatings that resist mechanical and weather effects is a challenging problem and involves numerous difficulties.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide improved articles having a polychromatic surface with sharply defined color boundaries. The polychrome surface may be a drawing or a portrait or miniature, in a wide color range and, if necessary, with half-tones. The polychrome surfaces are noted for their good mechanical strength, adherence, and resistance to moisture, acid or alkaline media, as well as to sharp temperature fluctuations and to radiation.

The above and other objects are accomplished by the provision of an article with a polychromatic picture imposed on the surface thereof, wherein on a solid dielectric layer coated with a film of a thickness of at least 500 Å of a unilaterally-conducting metal or of an alloy thereof there is produced a transparent anodic oxide film whose thickness varies from 100 to 6,000 Å at different areas of the article, thereby imparting different coloration to different areas of the picture due to light interference phenomena.

In the present context, the term "unilaterally-conducting metal" denotes a transition metal whose oxide film exhibits low asymmetric electron conduction.

The article surface may be bright or dull, or have a combination of bright and dull areas, depending upon the brilliance (degree of fineness) of the dielectric layer surface.

Where the degree of fineness of the dielectric surface layer is in the range of 11 to 14, the article in question will have a bright surface, whereas a dull surface will be obtained if the degree of fineness equals 7 to 10.

The process of manufacturing an article having a polychromatic picture imposed on its surface consists in depositing on a solid dielectric layer (substrate) a thin film of a unilaterally-conducting metal or of an alloy thereof, the film thickness being at least 500 Å. The thus obtained film is further broken into separate areas which conform to the shape of the picture to be reproduced, provision being made to insulate electrically each film area, followed by subjecting said areas to selective anodizing in Type I or II electrolytes at a constant current density of not greater than 10 mA/cm², the working voltage being in the 5 to 250 V range, depending upon the film area to be anodized.

It is preferred to effect the electric insulation of said film areas from one another by the provision of contour clearances.

The unilaterally-conducting metal may be selected from the group consisting of tantalum, niobium, and titanium.

Where a titanium film is subjected to anodic oxidation in a 0.01M solution of ammonium tartrate, the process should be carried out at a constant current density of 0.5–2.0 mA/cm², the desired coloration of selected film areas being attained with the following voltages applied:

Color	Voltage, V
brown	22 to 27
blue	33 to 36
light blue	40 to 45
yellow	65 to 73
red	93 to 98
green	115 to 150

BRIEF DESCRIPTION OF THE DRAWING

The invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawing in which:

FIG. 1 is a plan view which shows a dielectric substrate with the film of a unilaterally-conducting metal deposited thereon;

FIG. 2 is a similar view except that the film of unilaterally-conducting metal is broken by contour clearances which insulate each film area in conformity with the picture to be produced;

FIG. 3 shows the treatment of the article in an electrolytic cell, the article being seen in plan to show the varicolored film areas thereof; and

FIG. 4 is a cross-sectional view taken along line A—A in FIG. 3 showing an anodic film of variable thickness which serves for the coloration of specific film areas due to interference phenomena.

DETAILED DESCRIPTION

The method of manufacturing an article having a polychromatic picture imposed on the surface thereof involves three consecutive stages:

1) Depositing a thin film F of unilaterally-conducting metal, at least 500 Å thick, on the surface of a solid dielectric substrate S (FIG. 1).

When the article to be processed is made of a material which is devoid of dielectric properties, the surface of the article in question should be preliminarily coated with an insulating dielectric layer applied by any known technique, such as vacuum deposition, cataphoresis, or anodic oxidation.

2) Dividing the thusly obtained film of unilaterally-conducting metal or alloy thereof into separate areas in conformity with the picture to be reproduced, this operation being accomplished by the provision of contour clearances that bring about electric insulation of separate film areas F₁–F₇ from one another (FIG. 2).

3) Subjecting separate areas of the film to selective anodic oxidation for obtaining an oxide film of varying thickness which makes possible the coloration of each area to the desired color (FIGS. 3 and 4).

The first stage, i.e., the deposition of the film of a unilaterally-conducting metal or of an alloy thereof, such as tantalum or titanium, onto the solid dielectric substrate can be effected by any known technique, e.g., by cathode sputtering or by the pyrolysis of an organo-metallic compound.

The second stage of the process involves tracing the picture on the film F by the provision of contour clearances, which electrically insulate the separate areas of the film F₁-F₇, one from another. The clearances are formed by a variety of techniques, such as: mechanical milling with a copying device; chemical milling by covering the film areas with a protective varnish applied through a template, followed by etching the uncovered clearances; and photolithography.

The photolithographic technique consists in coating the film F with a light sensitive emulsion layer, followed by the application of the contour clearance pattern by contact printing, and thereafter developing the light sensitive emulsion so that the clearances to be etched become exposed, subjecting the intact emulsion to heat treatment for imparting chemical stability thereto, and, finally, chemically etching the contour clearances.

The third stage of the process consists in selective anodic oxidation of separate areas of the film F of unilaterally-conducting metal, wherein anodic polarization is effected in Type I or Type II electrolytes, provision being made for contacting each separate film area by means of a contact that leaves on the article being processed no traces discernible to the naked eye. The cathode is made from a self-passivating or noble metal that is conductive to uniform oxidation.

The Type I or II electrolytes are selected from 0.1M to 0.001M solutions of organic or mineral acids and salts in high-purity water (demineralized water having a resistivity of 0.5 Mohm or higher). The pH of the solutions used is maintained in the 4 to 7 range, the electrolyte temperature being maintained below 150° C, preferably 20°-30°. The anodizing process is conducted at a constant current density (i mA/cm² = const) of not greater than 10 mA/cm², preferably at a current density in the 0.1 to 1 mA/cm² range, provided the voltage increases spontaneously in the 5 to 250 V range, the voltage applied to different film areas being different so as to provide for the formation of oxide films having the desired thickness. Hence, the thickness of an oxide film on each area is controlled by the application of an appropriate voltage. Voltage selection is effected either visually or by means of calibration tables which correlate the voltage applied and the color obtained for each unilaterally-conducting metal-electrolyte combination. Anodic oxidation results in the formation of transparent oxide films of different thicknesses at different film areas, so that light interference phenomena produce a polychromatic effect on the surface of the finished article.

Presented below is a calibration table which correlates the voltage applied and color produced for tantalum, niobium, and titanium films subjected to anodic oxidation at a current density of 0.1 to 2 mA/cm² in a 0.01 M solution of ammonium tartrate acidified to a pH of 4-5.5.

Voltage, V	Color
5 to 27	brown
18 to 36	blue
24 to 45	light blue
40 to 80	yellow
76 to 100	red
110 to 155	green
85 to 180	red-purple
160 to 250	crimson red

It is to be noted that intermediate shades of the above-identified colors are obtainable at intermediate

values of voltages applied as compared to those indicated for pure colors.

In order to obtain superior quality films, it is expedient to effect the anodizing process at a constant voltage ($V = \text{const}$), this technique being conducive to elimination of oxide film defects. This treatment results in a sharp increase of the ohmic resistance of the film and in a concomitant improvement of its corrosion-resisting properties. The anodizing time is governed by the desired corrosion resistance of the resultant film, so that where the requirements are moderate, a process time of 5 minutes is adequate. If, however, stringent requirements are imposed on protective characteristics of the coating in question, the anodizing time at $V = \text{const}$ should be several scores of minutes, the mean anodizing period being 30-40 minutes.

The anodic oxidation process may be accomplished in a still bath or in a fluent electrolyte cell, the latter technique being preferable, inasmuch as electrolyte circulation makes possible filtration of the electrolyte.

Upon termination of the anodic oxidation process, the finished article is washed with high-purity water and dried at a temperature of 120°-150° C for at least 1 hour. Where recourse is had to a fluent electrolyte cell, it is expedient to wash the finished articles in the cell in question.

The surface of the finished articles may be bright, dull or a combination of both, these characteristics being dependent upon the brilliance of the dielectric material surfaces. In case the dielectric layer surface exhibits a degree of fineness equal to 11-14, the finished article would be bright, whereas for a degree of fineness in the 7-10 range, the article would be dull.

The present invention makes it possible to obtain an anodic coating noted for its good adherence to the metal film, as well as for its high mechanical strength under normal service conditions and at sharp temperature fluctuations in the -50° to + 150° C range, and also for its resistance to radiation. The present coating exhibits corrosion-resisting properties under tropical conditions. It is practically insoluble in organic or mineral acids or mixtures thereof, irrespective of concentration or proportions, except for hydrofluoric acid and salts thereof.

The manufacture of articles, according to the present invention, involves the consumption of an insignificant amount of the unilaterally-conducting metal.

The present method is conducive to large-scale production of the articles, according to the invention.

The fields of application of the present method are diverse and include the manufacture of souvenirs, badges, and jewelry (pendents, ear-rings, bracelets, and so forth,); finishing of instrument parts, insignia, emblems, and topographic layouts; production of large- and small-size panels, with or without a picture imposed thereon, for interior and exterior decorations of public buildings, etc., and also for making stained-glass panels.

The present invention is illustrated hereinbelow by the description of an exemplary embodiment thereof with reference to the manufacture of an article having a polychromatic picture on its surface.

EXAMPLE

An ordinary glass plate having a degree of surface fineness equal to 14 is degreased and dried at 300° C, and thereafter coated with a 1,500 Å thick metal film

by the cathode sputtering technique to yield a blank (FIG. 1).

In order to effect the cathodic sputtering of tantalum, recourse is had to the following process parameters:

preliminary evacuation $1-5 \times 10^{-6}$ mm Hg
working vacuum obtained by introducing argon into the system $1-2 \times 10^{-2}$ mm Hg
discharge voltage 3.2 - 3.5 kV
current 80 - 150 mA

Next, use is made of the photolithographic technique to transpose the picture to be reproduced on the thus obtained tantalum film. To do so, the metal film is degreased and thereonto is applied a 0.5 mm - thick light sensitive emulsion based on naphthoquinonediazide.

The light sensitive emulsion is applied by means of a sprayer and the layer thus obtained is dried in a dust-free chamber at a temperature of $70^{\circ}-80^{\circ}$ C. and thereafter maintained at said temperature for 15 minutes.

The plate coated with the light sensitive layer is next placed under a photographic template of the picture to be reproduced and exposed to ultra-violet light (wave length, 2,000 to 3,000 Å) for a period of 30 seconds, the photographic templates being made so that only the contour clearances are irradiated, while the surface of the separate areas which remain are unexposed. (Pertinent data on the manufacture of the template and preparation of the light sensitive emulsion are described below).

The emulsion applied to the irradiated areas, e.g., contour clearances, undergoes decomposition and can be readily removed by dipping the plate for 20-30 sec. into a 10 percent solution of trisodium phosphate. Next, the plate is washed with high-purity water until a neutral reaction is attained, then the plate is dried at a temperature of $70^{\circ}-80^{\circ}$ C for 15 minutes and thereafter subjected to heat treatment at a temperature of 120° C for a period of 5 min. in order to enhance the acid-resisting properties of the emulsion layer. Then, the plate is cooled and subjected to chemical milling (etching) along the contour clearances with an etchant consisting of a mixture of concentrated hydrofluoric and nitric acids in a ratio of 1:10 by volume. Etching is accomplished by submerging the plate into the etchant for a period of 20 to 30 seconds, followed by washing the plate with high-purity water.

The protective layer is removed from the unexposed areas of the tantalum film by an acetone-dioxane mixture (1:1 by volume). Now, the plate surface consists of separate areas that are electrically insulated from one another, the arrangement of said areas conforming to the image to be reproduced, as shown at F_1-F_7 in FIG. 2. The plate treated in the manner disclosed hereinabove can next be subjected to anodizing.

The anodic oxidation of areas 1, 2, and 3 of the tantalum film (FIG. 3) is conducted in an electrolytic cell furnished with a tantalum cathode 5. The electrolyte consists of 0.01M solution of ammonium tartrate maintained at a pH of 6. Current supply to the separate film areas is effected by means of tantalum rods 6, 7, and 8

bent at right angles and sharpened at the contact end. The current rating is 1.00 mA/cm², the voltage applied being selected in compliance with the color-voltage correlation Table for the tantalum film -electrolyte (ammonium tartrate) system -

- Area 1, blue color $V=36V$; $I_1=10$ mA; $\tau'_1=6$ min; $\tau''_1=20$ min. 10 cm²
Area 2, yellow color; $V=73V$; $I_2=3$ mA; $\tau'_2=12$ min; $\tau''_2=14$ min. 8 cm²
Area 3, red color $V=94V$; $I_3=12$ mA; $\tau'_3=16$ min; $\tau''_3=10$ min. 12 cm²

τ' - anodizing time at $i=\text{const}$;

τ'' - anodizing time at $V=\text{const}$.

When the anodic oxidation has been terminated, the plate is extracted from the cell, washed with high purity water and dried at a temperature of 100° C.

The light sensitive emulsion employed is prepared in a dark room (red light) by mixing 7.2 grams of novolak dissolved in 50 ml of dioxane with 4.6 grams of naphthoquinonediazosulfonate also dissolved in 50 ml of dioxane.

The photographic template is manufactured as follows. The picture to be reproduced is drawn to 10:1 scale on paper. The picture in question consists of three fields of dissimilar area separated from one another by contour clearances 0.5 mm wide. The three separate areas are inked, and the contour clearances remain uninked. The picture is photographed on a plate to yield a sharp positive print.

Depending upon the light sensitive emulsion used, which might be either positive or negative, the photographic template should be also positive or negative respectively.

In the present embodiment of the invention, use is made of the positive emulsion.

The finished article is colored blue, yellow and red. In view of the fact that the degree of fineness of the dielectric surface equals 14, the article will be bright.

What is claimed is:

1. An article with a polychrome picture imposed on the surface thereof, said article comprising a hard dielectric substrate, a film of a unilaterally-conducting metal or an alloy thereof on said substrate and divided into separate areas, and anodic oxide films on said areas of said metal film, which are different in thickness to provide different coloring of said areas with predetermined color boundaries due to light interference.
2. An article according to claim 1 wherein the metal oxide is of a metal from the unilaterally-conducting group of metals of the periodic table.
3. An article according to claim 1 wherein said separate areas of said metal oxide are electrically isolated from one another.
4. An article according to claim 1 wherein the metal film is of tantalum or titanium.

* * * * *