

[54] DECORATIVE ARTICLE AND METHOD OF MAKING SAME

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[51] Int. Cl.² **G03C 5/00**

[58] Field of Search **96/27 R, 36, 35, 38.1, 96/38.3, 34; 117/215, 34, 106 R**

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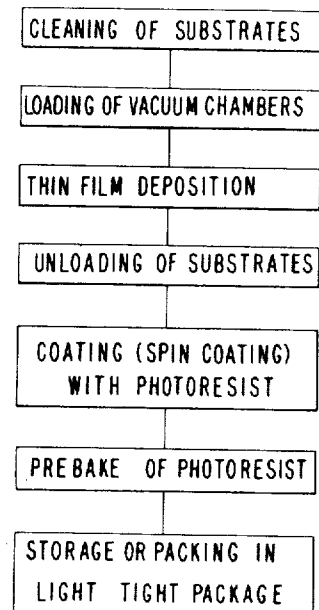
Attorney, Agent, or Firm—Limbach, Limbach & Sutton

[57] ABSTRACT

A decorative article and method of making same is disclosed wherein pictures are printed in a contrasting color on substrates such as ceramic, glass and the like.

7 Claims, 5 Drawing Figures

SUBSTRATE MATERIAL PREPARATIONS



PRINTING OF SUBSTRATES

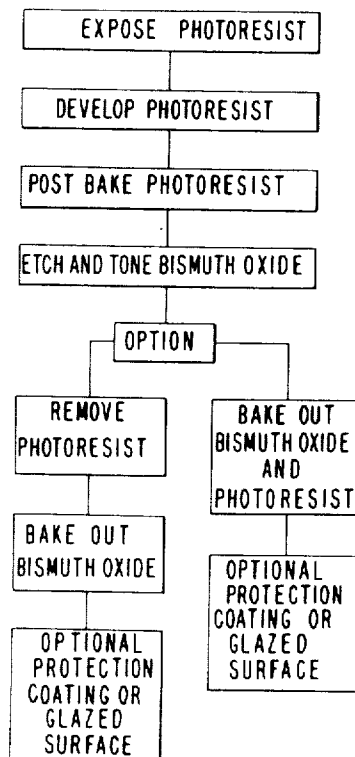


FIG. 1

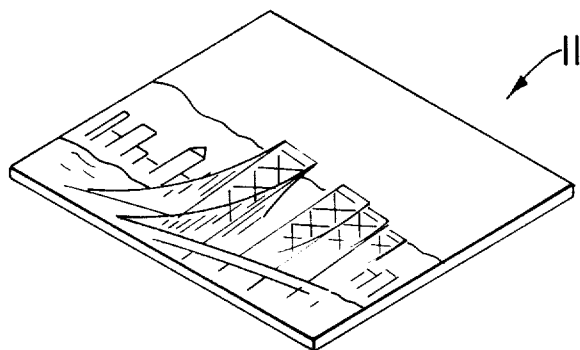
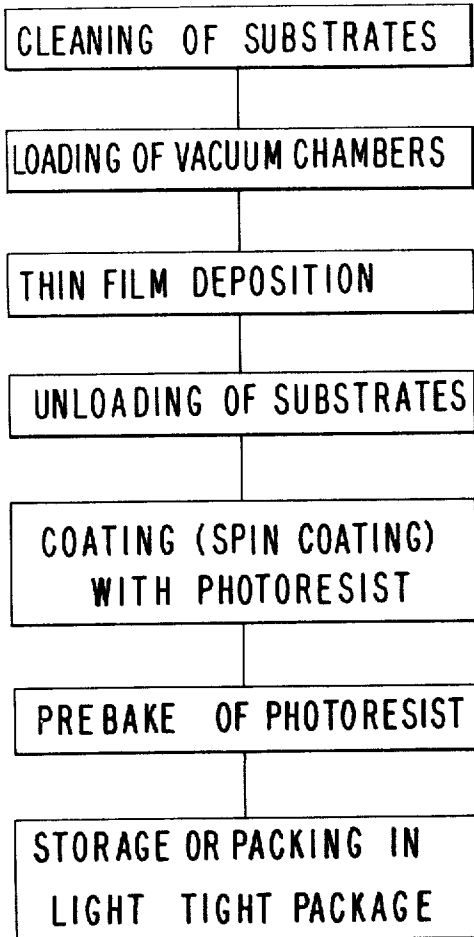


FIG. 2

SUBSTRATE MATERIAL PREPARATIONS



PRINTING OF SUBSTRATES

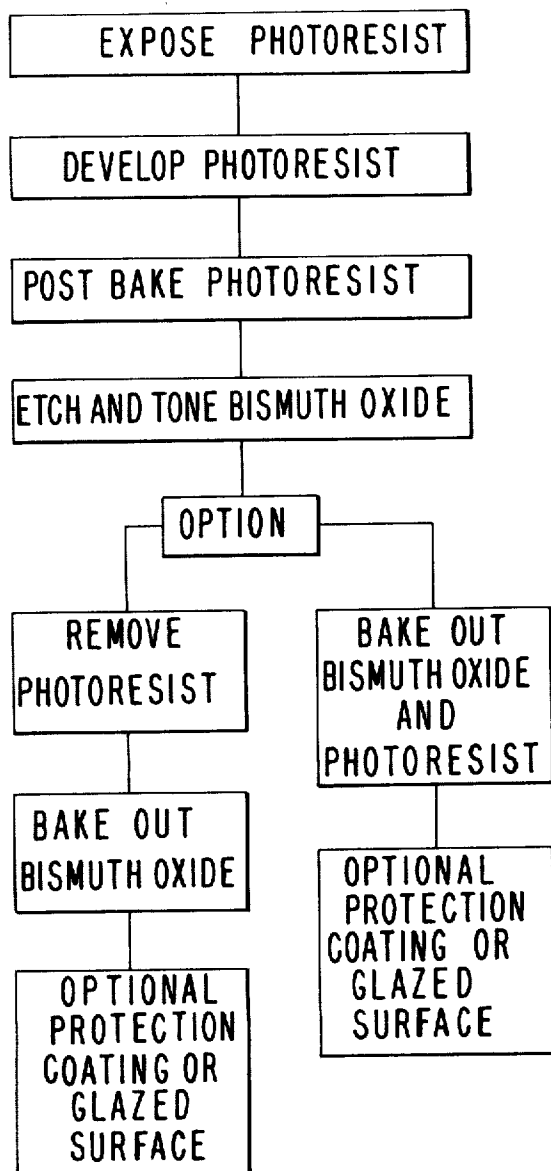


FIG. 3

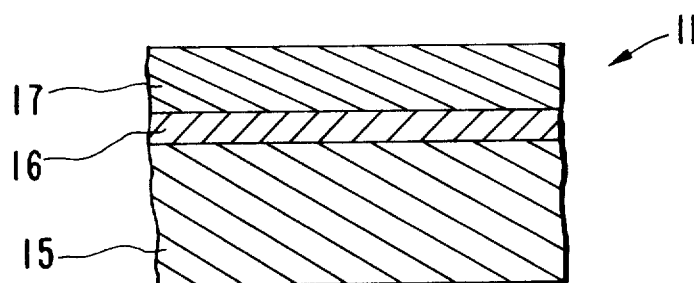


FIG. 5

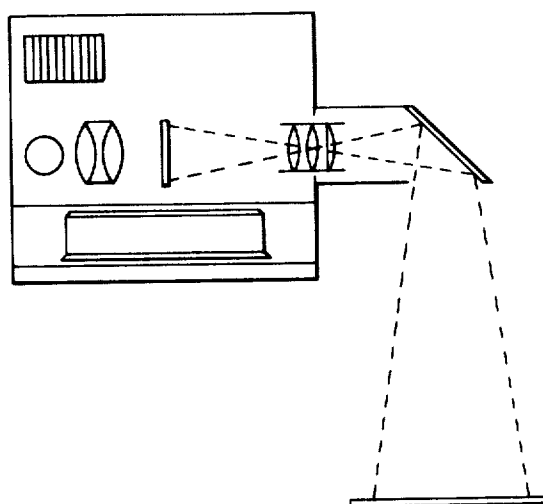
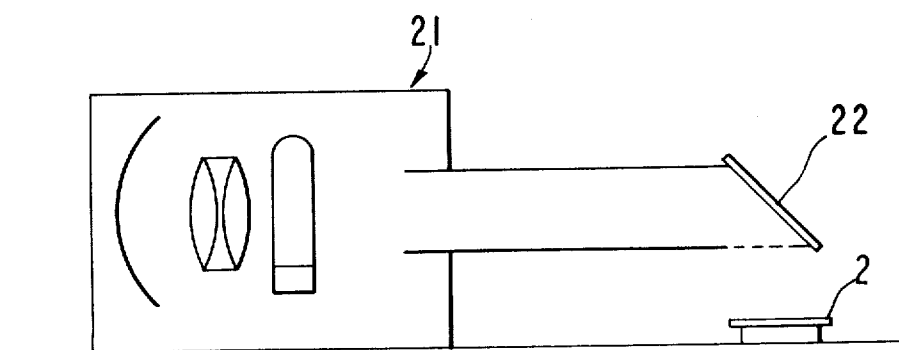


FIG. 4



DECORATIVE ARTICLE AND METHOD OF MAKING SAME

BACKGROUND OF INVENTION

This invention is directed in general to a decorative article and method of making same in the form of a picture in a contrasting color printed on a substrate such as ceramic, glass etc. The article provides a consumer product as jewelry, ornaments and the like.

The conventional way of decorating consumer type ceramics, porcelain and glasses is by printing, brush painting or silk screening of patterns on the substrates or materials. After the pattern has been established, the work is usually glazed by firing it in a kiln and the product is finished. Often times the printing or painting is painstakingly done by hand or the master silk screen is produced by hand resulting in a very expensive product. Usually, the cost is prohibitive where a single article with a unique pattern or print is desired. Also there is a need for a consumer product where the prints are produced with much more precision than presently commercially available and yet still made available at a price competitive with decorative ceramics, porcelain and chinaware.

The object of the present invention is to provide a decorative article and method for making same for producing pictures on substrates in contrasting color and utilizing photographic techniques. As used herein "contrasting color" or "color" is used to include achromatic colors such as black, white and grays as well as chromatic colors.

In accordance with one aspect of the present invention the decorative article is provided by first layering the substrate with an image forming material that will result in a color contrast picture on the substrate and then coating the layered substrate with a photosensitive material. The photosensitive material is exposed with a picture which is developed to then provide a mask for removing undesired image forming material defined by the picture leaving a contrasting color picture of image forming material on the substrate.

The substrate materials which have been used are ceramics, sapphire, glass, gold and metal-coated, such as gold-coated, ceramics.

Good image forming materials are bismuth oxides such as bismuth trioxides of the yellow rhombic, white rhombic and gray-black cubic crystalline forms. A highly desirable combination is bismuth trioxide of the gray-black cubic form on a ceramic (alumina) substrate producing a highly desirable black on white article.

Since photographic techniques are utilized to form the picture on the substrate, the article can be formed quickly and easily by unskilled labor thereby producing an economical consumer product. Also by using photographic techniques, a precisely defined picture can be reproduced on the substrate.

Other colors or color combinations are possible with selected material. Bismuth oxide then can be coated on or coated by gold, silver or platinum. Similarly, by variations in the manufacturing techniques, color differences can be produced using the same materials.

These and other features and advantages will become more apparent upon a perusal of the following specification taken in conjunction with the accompanying drawings wherein similar characters of reference refer to similar structures in each of the several views.

FIG. 1 is an enlarged perspective view of an article produced in accordance with the present invention.

FIG. 2 is a block diagram flow chart showing the steps performed with the present invention.

FIG. 3 is an enlarged sectional view through an article prepared for printing in accordance with the left hand side of FIG. 2.

FIG. 4 is an elevational view schematically illustrating one simple technique for contact printing the picture onto the substrate.

FIG. 5 is a top view of a slide projector illustrating slide projection illumination of a decorative article produced in accordance with the present invention.

While the present invention has many applications to articles of different sizes, shapes and materials for substrates and many different coating materials, a unique black and white decorative article is produced with the present invention and will be described as a preferred embodiment.

Referring now to the drawing there is shown in FIG. 1 an article 11 such as a small piece of jewelry as a cuff link or tie tack provided with a printed picture thereon. In the embodiment illustrated the substrate or white material on which the picture is printed is alumina and the black portions of the picture are formed of bismuth oxide, specifically bismuth trioxide of the gray-black cubic crystalline form. "Bismuth oxide" is used herein to described any of the oxides of bismuth and as more particularly defined. Bismuth trioxide is a suitable material and has several crystalline forms, yellow rhombic crystalline form having a melting point of 820°C, white rhombic crystalline form having a melting point of 860°C, and gray-black cubic crystalline form having a transition point of 704°C. It is possible to start with any one of these crystalline forms and by proper evaporation end up with a desired final coating. As another alternative material, bismuth pentoxide of the dark red or brown crystalline form can be utilized.

Referring to FIG. 2, the method for forming the article 11 includes first cleaning the alumina substrate and loading the substrates in a vacuum evaporation chamber of any of the commercially available types for vacuum evaporation at a level of approximately 10^{-5} torr level or better. A thin layer of bismuth trioxide of the gray-black cubic crystalline form can be produced by starting with bismuth trioxide white rhombic crystalline form powder placed in an alumina coated boat in the vacuum. With proper evaporation temperature and rate, the deposit on the substrate will end up with the cubic black crystalline structure. This black coating provides good black prints and adheres well to white ceramics (for black and white prints), on gold or gold coated substrates (black on gold prints) and black on other colors depending upon the color of the substrates. Bismuth oxide adheres well to ceramics, sapphire and glass as well as metals such as gold, silver and platinum, which can be provided in a desired pattern on one of the aforementioned substrates. It is also possible to coat the gold, silver or platinum on the bismuth oxide for a gold, silver or platinum picture on black.

With different evaporation temperatures and rates and different boat materials such as tantalum, tungsten and molybdenum it is possible to obtain depositions of bismuth oxide in colors from black to red-brown. After vapor deposition in thicknesses of typically between 0.4 and 1 micron the vacuum in the chamber is broken and the coated substrates unloaded.

Next, the bismuth oxide surface is coated with an appropriate photoresist material for defining the picture on the article. Where the picture is formed from a photo negative, a negative type photoresist material is appropriate or where a slide is utilized, a positive type photoresist material is utilized. The photoresist material can be applied in one of the well known techniques such as dipping, spraying or spinning. For sharp, fine prints spin coating works very well. The photoresist is prebaked in place and then the substrates are packaged in a light tight manner for storage or shipment to the customer who will print upon them.

FIG. 3 shows an enlarged elevational sectional view taken through one of the prepared substrates showing the alumina substrate 15 provided with the dark, thin film coating 16 of bismuth trioxide which is in turn coated with the photoresist coating 17.

For printing the picture on the prepared substrates a standard photo negative, slide or glass mask for contact printing or production printing can be used, and normal photo exposure procedures are then followed.

An economical way of printing is the use of a standard slide projector 21 as shown in FIG. 4 and wherein the projection light beam is directed by an angled mirror 22 onto the photo negative 23 positioned in contact with and on top of the photo-resist layer. After exposure for the appropriate length of time, the exposed photoresist material is processed through developer and a post exposure bake. After the photoresist has been processed the substrate is then placed in a dilute acid etchant to etch the dark bismuth oxide in the appropriate processed region of the photoresist. The proper etching time, combined with the proper photoresist spinning rate, exposure and development times will result in a very sharp print. By over etching a silhouette type effect can be obtained. Where a gold (or silver or platinum, etc.) layer has been provided underneath or on top of the bismuth oxide, an increased post bake temperature diffuses the bismuth oxide into the gold and after etching, the gold or gold coated substrate gives the effect of an antique gold color.

As illustrated in FIG. 2 the photoresist can optionally be first removed in a standard photoresist remover, or with the photoresist left on in place the substrate and etched pattern are fired at appropriate temperatures such as 150°C (or higher) for at least 15 minutes for bakeout of the bismuth oxide. The bismuth oxide then adheres firmly to the substrate.

As an added precaution, a plastic spray or glaze can be used, although without these extra coatings the bismuth oxide appears to be stable and permanent. When glazes are used, firing temperatures should preferably be under 250°C and therefore the glazes used are basically soft glazes or solder glazes.

It will be appreciated from the above description that it is relatively easy to print on both sides of a flat substrate or around a curved surface.

The method described above is very economical even on a one item basis, and where many identical items are desired, the same print is "stepped and repeated" on a large substrate and the substrate cut into smaller individual pieces each with the desired picture.

It is believed that the invention has been described above in sufficient detail to enable one skilled in the art to follow the method and produce articles in accordance with this invention. For further illustration, the following example is given of one article made in accordance with this invention.

A thin ceramic plate 99.5% pure alumina with a surface finish of 10 microinches or better is first cleaned utilizing the following steps (a) hot trichloroethylene (TCE) degreaser for two minutes, (b) hot acetone for five minutes, (c) boiling TCE for five minutes, (d) blown dry with nitrogen, (e) rinsed in de-ionized water, (f) blown dry with nitrogen, (g) hot nitric acid for five minutes, (h) rinsed in de-ionized water for ten minutes, (i) blown dry with nitrogen, (j) hot isopropyl alcohol for five minutes, and (k) blown dry with nitrogen. Clean substrates are loaded in a vacuum chamber evacuated to better than 2×10^{-5} torr and wherein bismuth trioxide positioned in alumina coated boat is evaporated onto the substrates to a thickness of between 0.4 and 1 micron. A photo-resist coating of the KMER-type for a photonegative is spin coated on the substrate at a spinning speed of 2000 r.p.m. for thirty seconds and prebaked in accordance with the instructions of the manufacturer, i.e., 180°-190°F. for fifteen minutes for the KMER. These coated substrates were wrapped in light-tight packages and hermetically sealed. The picture was printed on the photo-resist material using a 500 watt projector lamp for making a contact print. With photonegatives of different qualities, exposure times of from six seconds to one minute were utilized. Next, the photo-resist was developed in accordance with the manufacturer's instructions of one and one-half minutes in developer, thirty seconds in rinse, ten to fifteen seconds in isopropyl alcohol and blown dry in nitrogen. The ceramic and developed photo-resist were post baked at 350°F. for fifteen minutes and cooled to room temperature. The article was then etched and the bismuth oxide toned in dilute acid according to visual preference and using one part nitric acid to three parts water for the etchant and one part nitric acid to five parts water for toning with the article thereafter washed in water and dried. The final step was a bake out of the bismuth oxide and photo-resist in air at 400°F. for thirty minutes in an oven.

Articles produced in accordance with this invention cannot only be decorative jewelry and the like but can actually be projected as a slide if the substrate is translucent and mechanically strong. For example, ceramic 10 mils or less thick have been utilized to produce a black on white article as described above which can then be illuminated in a standard slide projector for projection of the image. Ceramics even thicker can be utilized. Such utilization is illustrated in FIG. 5 wherein a standard slide projector 31 is schematically shown and provided with a correction mirror on the front thereof to correct the reversed image.

Ceramic slides of this type can withstand much higher temperatures than can conventional slides. While the slide can even be as thick as 25 mils, the thicker slide results in less image brightness.

While the invention has been described principally with respect to black and white pictures, color pictures as decorative articles and photo-slides can be produced. For example, the blue for the color picture can be achieved using cobalt.

We claim:

1. A method of making a decorative article comprising evaporating a layer of image forming material of an oxide of bismuth for a resulting layer of bismuth trioxide of gray-black cubic crystalline form on a substrate,

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coating the layered substrate with a photo sensitive material,
 exposing the photo sensitive material with a picture,
 developing the picture exposed photo sensitive material and

etching away the undesired bismuth trioxide of gray-black cubic crystalline form defined by the picture thereby leaving the image forming bismuth trioxide of gray-black cubic crystalline form on the substrate.

2. The method of claim 1 wherein the layering step includes evaporating a layer of image forming material of bismuth trioxide for a resulting layer of bismuth trioxide of gray-black cubic crystalline form on an alumina substrate.

3. The method of claim 1 wherein the layering step includes evaporating a layer of image forming material of bismuth trioxide for a resulting layer of bismuth trioxide of gray-black cubic crystalline form on a metal coating on an alumina substrate.

4. The method of claim 1 wherein the layering step includes evaporating a layer of bismuth trioxide of yellow rhombic crystalline form on the substrate.

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5. The method of claim 1 wherein the layering step includes evaporating a layer of bismuth trioxide of white rhombic crystalline form on the substrate.

6. A method of making a decorative article comprising the steps of:

evaporating a layer of image forming material of bismuth trioxide for a resulting layer of bismuth trioxide of gray-black cubic crystalline form for a resulting color contrasting picture on a thin alumina substrate,

coating the layered sheet with a photoresist material, preexposure baking of the photoresist, photographically exposing the layered substrate with a picture,

developing the exposed photoresist, post exposure baking the photoresist, etching the undesired image forming bismuth trioxide layered on the alumina substrate and post etch baking the assembly.

7. The method of claim 6 wherein the layering step includes applying bismuth trioxide of a gray-black cubic crystalline form on a metal coating on the alumina substrate.

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