March 5, 1963 R. W. GILBODY ET AL 3,080,232

METHOD FOR PHOTOGRAPHICALLY PRODUCING ELECTRICAL CONDUCTOR PATTERNS INSIDE A HOLLOW OBJECT

Filed Nov. 29, 1957 2 Sheets-Sheet 1

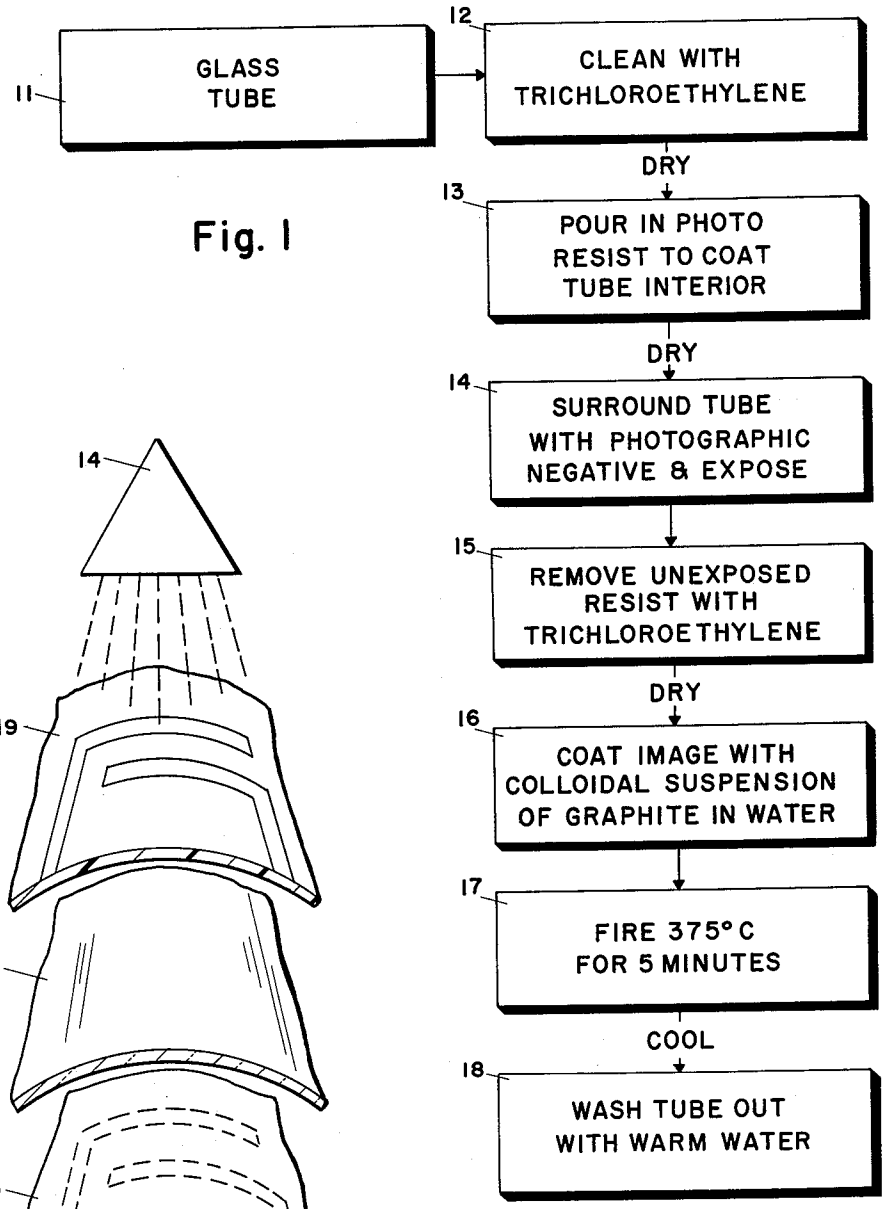


Fig. 1

Fig. 2

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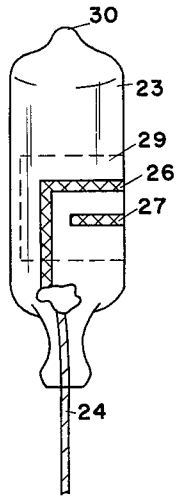


Fig.3

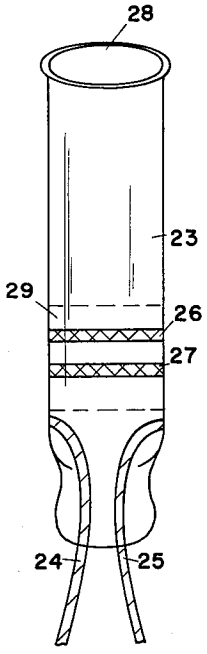


Fig.4

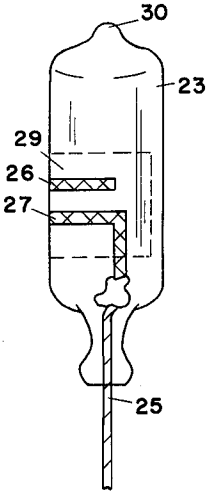


Fig.5

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United States Patent Office 3,080,232 Patented Mar. 5, 1963

3,080,232

METHOD FOR PHOTOGRAPHICALLY PRODUCING ELECTRICAL CONDUCTOR PATTERNS INSIDE A HOLLOW OBJECT

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6 Claims. (Cl. 96—35)

This invention relates to an article of manufacture and improved method of marking or printing on surfaces transparent to radiant energy and more particularly to miniature photo-conductor tubes and a method of printing electrodes on the interior surface thereof.

One type of prior art photo-conductor tubes has electrodes which are manually applied to the inside surface of the tube envelope with a brush. A disadvantage of such an arrangement is that the resulting tubes must be at least large enough to lend themselves readily to the maneuvering of a brush within the cell blank or unsealed tube. A further disadvantage of such a method is that it makes uniformity and mass production of such tubes quite difficult. While the present invention is subject to a wide range of applications, it is especially suited for use in printing circuits inside small diameter transparent tubes and will be particularly described in that connection.

It is an object of this invention, therefore, to provide an improved method of printing circuits on transparent surfaces.

Another object of this invention is to provide a simple and inexpensive method of producing a pattern of any desired configuration on a surface transparent to radiant energy which does not lend itself readily to the manual application of said pattern.

A further object of this invention is to provide a method of printing electrodes on the inside surface of photo-conductor tubes, to enable unlimited miniaturization of such tubes.

In accordance with the invention, there is provided a method of marking in a desired pattern a surface of an object having an area transparent to radiant energy. The method comprises coating the surface with a compound sensitive to radiant energy and exposing the compound coating to radiant energy passing through the transparent area to produce a latent image of a desired configuration on the compound coating. The undesired or excess compound coating is removed to leave the desired marking pattern.

In accordance with the invention there is further provided, as an article of manufacture, a miniature photo-conductor tube. The tube comprises an envelope transparent to radiant energy and has electrodes printed on its inside surface by means of a radiant energy sensitive compound exposed to an image projected through the transparent tube envelope. A lead sulphide coating covers the printed electrodes and the area therebetween. A pair of conducive leads are connected to the electrodes and pass through the tube envelope for transmitting the energy from the electrodes to a circuit.

For a better understanding of the present invention, together with other and further objects thereof, reference is made to the following description taken in connection with the accompanying drawings and its scope will be pointed out in the appended claims.

In the drawings:

FIG. 1 is a flow chart illustrating the process of printing a conductive pattern on the inside surface of a glass tube in accordance with the invention;

FIG. 2 is a perspective view partly in section of a glass tube illustrating the exposure of a coating of the inside surface to radiant energy.

FIG. 3 is a side elevation view of a sealed photo-conductor cell having electrodes printed therein in accordance with the principles of the invention.

FIG. 4 is a side elevation view of an unsealed cell blank similar to that of FIG. 3, but rotated 90°; and

FIG. 5 is a side elevation view of the cell blank of FIG. 3 rotated through an angle of 180°.

Referring now to the drawings and with particular reference to FIGS. 1 and 2, there is here illustrated the process for depositing or printing a conductive pattern on the inside surface of a glass tube **11**. The process is described in steps as follows:

(1) Cleaning the glass tube **11** with tri-chloroethylene **12** and permitting the tri-chloroethylene to evaporate until the tube is dry.

(2) Pouring in a photo-resist **13**, such as the cinnamic acid ester of polyvinyl alcohol, and thoroughly coating the tube interior with the resist.

(3) Pouring out any excess resist **13**, and permitting the resist to dry.

(4) Surrounding glass tube **11**, with a photographic negative **19**, as shown in FIG. 2.

(5) Exposing the resist through the negative to an appropriate light source **14**.

(6) Removing any unexposed resist with tri-chloroethylene to evaporate **15**.

(7) Coating the image with the colloidal suspension of graphite in water, such as Aquadag made by the Acheson Colloids Corporation of Port Huron, Michigan, 16. (The colloidal graphite may be incorporated in the photo-resist at the outset to eliminate this step in the process. This is not necessarily advantageous, however, as the black pigment absorbs so much light that it acts as a light filter and prevents exposure of the photo-resist.)

(8) Firing at 375° C. for five minutes followed by gradual cooling to prevent breakage of the glass **17**.

(9) Washing out glass tube **11** with warm water **18**.

Considering now the process just described and referring to FIGS. 3, 4 and 5, there is here illustrated a photo-conductor tube embodying the teaching of this invention. The cell blank **23** is preferably formed from a glass tube having an outside diameter of, for example 0.390 inch, and an inside diameter, for example, of 0.360 inch. A pair of leads **24** and **25**, formed, for example from nickel 0.020 of an inch in diameter, are then fused to the tube. The ends of leads **24** and **25** extending into the tube are curved to follow the tube contour as shown, and silver pasted in place. The leads **24** and **25**, protruding outside the cell blank **23**, are cut to an appropriate length, as for example 1½ inches. Electrodes **26** and **27** shown cross-hatched are then printed inside cell blank **23** as described above. The photo-resist **13** for coating the inner surface of cell blank **23** is introduced through the open end **28**, exposed to light **14** and developed in accordance with the above described process. The electrode composition resulting from this process possesses good conductivity characteristics and exhibits a bond strength between the carbon and the glass which is far superior to bond strengths achieved by manual application of the colloidal graphite. The electrodes **26** and **27** are subsequently coated, for example with a lead sulphide or other light sensitive film, covering the area **29** encompassed by the dotted line in FIGURES 3, 4 and 5.

While applicant does not intend to be limited to any particular tube shapes or sizes in the embodiment of the invention just described, there follows a set of overall dimensions which have been found to be particularly suitable for a miniature photo-conductor tube.

Overall length	15/16 inch.
Distance from top of electrode 26 to tip 30 of cell blank	9/16 inch.
Width of electrodes 26 and 27	1/32 inch.
Distance from bottom of electrode 27 to bottom of cell blank	9/16 inch ±1/32.
Longitudinal thickness of fused bottom portion of cell blank 23	15/64 inch.
Width of flattened sealed bottom portion	1/8 inch.

These tolerances are readily maintained by printing of the electrodes in the manner just described. The relative position of photographic negative **19**, tube **11**, photo-resist coating **13**, and light source **14** are illustrated in the exploded view of FIGURE 2. It should be noted, however, that to obtain uniform results negative **19** should, during exposure, be in physical contact with the outside of tube **11** just as resist coating **13** is in contact with the inner surface of tube **11**.

It is apparent from the above considerations that a carbon configuration of the type described could be electroplated or a metallic suspension, as for example colloidal silver, gold, or copper, could be used with a photo resist instead of carbon. Likewise, any number of varieties of radiant energy sources could be used in combination with an appropriate photo resist. For example, materials can be used as photo resists that will polymerize when exposed to radiant energy such as ultraviolet light, gamma radiation, microwave energy and X-rays. Radiant energy of these types can be focused into desired pattern by using a material impervious to the energy type but apertured in the appropriate configuration.

A further use for the process of this invention lies in the fact that opaque configurations may be accurately deposited in places where they are resistant to wear. An example of this would be the printing of a thermometer scale on the inside surface of the thermometer tube. Other examples are the printing of numerals on the inside surface of tiny watch crystals, printing scales on scientific instruments and printing reticles.

While there has been described what is at present considered to be the preferred embodiment of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. A method of providing electrical conductors in a desired conductive pattern on the inside surface of a hollow object having an area transparent to a radiant energy source which comprises: coating said surface with a photo-resist sensitive to radiant energy; disposing a model image between said radiant energy source and said transparent area; exposing said photo-resist coating to said radiant energy passed through said model image and said transparent area to produce a latent image in a desired configuration on said photo-resist coating; removing the unexposed photo-resist coating to leave said surface marked in said desired pattern; coating said pattern with a colloidal suspension of graphite; baking said object until said graphite particles adhering to said photo-resist coating are fixed; and washing off any unadhering graphite particles.

2. A method of providing electrical conductors in a desired conductive pattern on the inside surface of a hollow object having an area transparent to a radiant energy source which comprises: coating said surface with a photo-resist sensitive to radiant energy; disposing a model image between said radiant energy source and said transparent area; exposing said photo-resist coating to said radiant energy passed through said model image and said transparent area to produce a latent image in a desired configuration on said photo-resist coating; removing the unexposed photo-resist coating to leave said surface marked in said desired pattern; coating said pattern with a colloidal suspension of graphite; baking said object until said graphite particles adhering to said photo-resist coating are fixed; washing off any unadhering graphite particles; and plating said conductive pattern with a metal.

3. A method of providing electrical conductors in a desired conductive pattern on the inside surface of a hollow object having an area transparent to a radiant energy source which comprises: coating said surface with a compound sensitive to radiant energy which comprises substantially fully esterified cinnamic acid ester of polyvinyl alcohol; disposing a model image between said radiant energy source and said transparent area; exposing said compound coating to said radiant energy passed through said model image and said transparent area to produce a latent image in a desired configuration on said compound coating; removing the unexposed compound coating to leave said surface marked in said desired pattern; coating said pattern with a colloidal suspension of graphite; baking said object until said graphite particles adhering to said compound coating are fixed; and washing off any unadhering graphite particles.

4. A method of providing electrical conductors in a desired conductive pattern on the inside surface of a hollow object having an area transparent to a radiant energy source which comprises: coating said surface with a compound sensitive to radiant energy which comprises substantially fully esterified cinnamic acid ester of polyvinyl alcohol; disposing a model image between said radiant energy source and said transparent area; exposing said compound coating to said radiant energy passed through said model image and said transparent area to produce a latent image in a desired configuration on said compound coating; removing the unexposed compound coating to leave said surface marked in said desired pattern; coating said pattern with a colloidal suspension of graphite; baking said object until said graphite particles adhering to said compound coating are fixed; washing off any unadhering graphite particles; and plating said conductive pattern with a metal.

5. A method of providing electrical conductors in a desired conductive pattern on the interior surface of a hollow cylindrical tube having an area transparent to a radiant energy source and substantially small inside diameter which comprises: coating said surface with a compound sensitive to radiant energy which comprises substantially fully esterified cinnamic acid ester of polyvinyl alcohol; disposing a model image between said radiant energy source and said transparent area; exposing said compound coating to said radiant energy passed through said model image and said transparent area to produce a latent image in a desired configuration on said compound coating; removing the unexposed compound coating to leave said surface marked in said pattern; coating said pattern with a colloidal suspension of graphite; baking said object until said graphite particles adhering to said compound coating are fixed; and washing off any unadhering particles.

6. A method of providing electrical conductors in a desired conductive pattern on the interior surface of a hollow cylindrical tube having an area transparent to a radiant energy source and substantially small inside diameter which comprises: coating said surface with a compound sensitive to radiant energy which comprises substantially fully esterified cinnamic acid ester of polyvinyl alcohol; disposing a model image between said radiant energy source and said transparent area; exposing said compound coating to said radiant energy passed through said model image and said transparent area to produce a latent image in a desired configuration on said compound coating; removing the unexposed compound coating to leave said surface marked in said pattern; coating said pattern with a colloidal suspension of graphite; baking

said object until said graphite particles adhering to said compound coating are fixed; washing off any unadhering graphite particles; and plating said conductive pattern with a metal.

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