United States Patent [19]

Hammond et al.

[11] **3,918,977**

[45] **Nov. 11, 1975**

[54] **METHOD FOR COATING METALLIC STRIPS**

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[22] Filed: **Aug. 13, 1973**

[21] Appl. No.: **387,762**

Related U.S. Application Data

[63] Continuation of Ser. No. 289,139, Sept. 14, 1972, abandoned.

[52] **U.S. Cl.** ..... **96/86 R**; 96/93; 96/115; 427/435

[51] **Int. Cl.**[2] **G03C 1/94**

[58] **Field of Search** ..... 117/34, 127, 128.4; 96/115, 86 R, 36, 93; 427/435

[56] **References Cited**

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[57] **ABSTRACT**

A method is disclosed whereby a uniformly thin coating of an aqueous solution of photosensitive material is applied to at least one surface of a metallic strip moving in a substantially vertical direction. The strip is withdrawn from a container having the solution therein whereupon it moves in a substantially vertical direction for a predetermined time period to permit the coating on the strip to flow in a substantially downward direction in such a manner so as to achieve uniformity of thickness. Thereafter, the strip is exposed to a heat source and the coating is dried thereon. Formulations for solutions suitable for use with this method are also disclosed.

5 Claims, No Drawings

METHOD FOR COATING METALLIC STRIPS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of Ser. No. 289,139, filed Sept. 14, 1972, now abandoned and assigned to the assignee of the present invention. The original assignment was recorded on Sept. 14, 1972, Reel 2892, Frame 727.

The method as disclosed in this application can be utilized with the apparatus described in U.S. patent Application Ser. No. 289,180 filed Sept. 14, 1972, entitled "Apparatus and Method for Coating Metallic Strips" and assigned to the assignee of the present invention.

BACKGROUND OF THE INVENTION

This invention relates to coating methods and more particularly to a method for applying a substantially uniform coating to a metallic strip moving in a substantially vertical direction. Even more particularly, this invention relates to the application of a thin uniform coating of photosensitive material to at least one surface of a vertically moving metallic strip which is eventually to be fabricated into metallic articles such as aperture masks for use in color cathode ray tubes. The method as described herein is believed to be new and consists of the first of several steps involved in producing such aperture masks or similar articles.

After completion of the coating step in the production of aperture masks, the metallic strip is usually moved to a photoprinting station where predetermined portions of the coating on the strip are exposed. After the removal of either the exposed or unexposed portions, the strip is subjected to an etching step wherein echtant solutions are usually sprayed to remove the unprotected portions of the strip, thereby leaving a designated pattern of apertures on the strip. As is known in the art, the strip is then segmented with each of the individual segments thereafter formed and aligned with the internal cathodoluminescent screen of a color cathode ray tube. The purpose of this mask in the finished tube is to aid in directing electron beams to preestablished areas of phosphor dots on the above-mentioned screen.

Heretofore, the application of photosensitive coatings on metallic strips to be utilized in the above-described manner have been achieved while the strip was aligned in a vertical position and moving in a substantially horizontal direction. As described in detail in U.S. Pat. No. 2,791,514, the coating material is applied in liquid form to the top marginal edge of the thoroughly cleaned metallic web and allowed to flow downward freely over both faces of the webbing. This is accomplished as the metal webbing travels edgewise through a coating station. On far too many occasions, however, the coating thickness at the bottom of the strip proved greater than at the top, usually the result of thicker concentrations of coating material accumulating at the bottom and not being able to dry at a sufficient rate with those concentrations along the upper surfaces. As can be appreciated, in precisely defined articles such as aperture masks, this difference in thicknesses can result in misalignment of the photoprinters during the photoprinting phase and thereby produce uneven patterns of exposed or unexposed areas. Additionally, non-uniform thicknesses of the coatings can result in unequal rates of etching of the metal, thereby

resulting in some openings being larger or smaller than desired.

Another prior art method involves dipping individual metallic panels into photosensitive solution, withdrawing the panels and thereafter allowing them to dry. However, Applicants have found that this process also yields the "coating wedge" described above wherein the coating at the bottom is thicker than at the upper areas of the panel. Still another prior art method incorporates a press apparatus which presses a dried photosensitive material having a polymeric backing onto the metallic strip. While this process eliminates the coating wedge, it does not prove satisfactory in obtaining relatively thin coatings on the strip and is, therefore, excessively time consuming and expensive.

It is believed, therefore, that a method for applying a substantially uniform thin coating of photosensitive material to a substantially vertically moving metallic strip which would overcome the disadvantages of prior art methods would constitute an advancement in the art.

OBJECTS AND SUMMARY OF THE INVENTION

It is, therefore, a primary object of this invention to provide a method for applying a relatively thin uniform coating of photosensitive material to at least one surface of a moving metallic strip.

It is a further object of this invention to provide a method for applying said coating as the metallic strip moves in a substantially vertical direction.

It is a still further object of this invention to provide a method for applying the above coating which obviates the previously described disadvantages of prior art methods.

It is an even further object of this invention to provide formulations of photosensitive coating solutions which are suitable for use with the coating method described herein.

In accordance with one aspect of this invention, there is provided a method for applying a substantially uniform coating of an aqueous solution of photosensitive material to at least one surface of a vertically moving metallic strip. This method comprises the step of withdrawing the strip in a substantially vertical direction from the aqueous solution, providing a predetermined time period in which the photosensitive material on the surface of the strip is permitted to flow downward in such a manner so as to achieve uniformity of thickness, and then exposing the photosensitive material on the strip to an established heat source whereby the material is dried.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above description of one of the aspects of the invention.

Referring now to the invention with greater particularity, it has been experimentally determined that vertically moving metallic strips can be uniformly coated with aqueous solutions of photosensitive materials by proper co-ordination of the two basic components for forming such coatings — (1) the coating solution itself, and (2) the vertical withdrawal time period before the

coating is dried. Basically speaking, Applicants permit the undried coating on the vertically moving strip to flow substantially downward and thereby achieve uniformity of thickness just prior to the coating being exposed to an established heat source. By providing an aqueous solution of photosensitive material, Applicants achieve this uniform coating as a result of substantially controlling the viscous properties of the solution as it is on the strip. More specifically, as the strip to be coated leaves the desired solution and is yet to be exposed to a heat source, two occurrences result. First, because the solution is aqueous, some evaporation occurs which thereby increases the viscosity of the undried coating. Secondly, a wet film occurs which permits the coating to flow downwardly and substantially reduces the possibilities of irregularities forming on the coating surface. When this substantially uniform coating is exposed to the heat source, once again two occurrences result. Firstly, the heaters reduce the solution's viscosity, thereby increasing its ability to flow. Secondly, the heaters cause evaporation of the solvents in the solution (the primary being water) which in turn increases the viscosity of the coating solution. It is obvious, therefore, that to achieve a uniform coating, a relatively delicate balance must be maintained during this heater exposure period so that the temperature rise of the coating solution is offset by the evaporation of the solvent, or solvents, in the solutions. To achieve this balance, Applicants have experimented with a variety of formulations of aqueous solutions of photosensitive materials and selectively determined several which are suitable to the above-described method. Combining the properties of these solutions with prescribed withdrawal rates and periods to permit the undried coatings to achieve uniformity of thickness by downward flow has resulted in several successful uniform coatings of this strip.

To more fully illustrate the present invention, the following detailed examples are presented. All parts, proportions and percentages are by weight unless otherwise specified.

EXAMPLE 1

Tests were run in which commercially available fish glue comprising about 20 to about 29% of the solution was mixed with water comprising about 40 to 62% of the solution. An alcohol, isopropanol, was also added and comprised about 16 to 33%. As a sensitizer, ammonium dichromate, $(NH_4)_2Cr_2O_7$, was added at a ratio of substantially between 80 and 130 grams per liter of fish glue. The specific gravity for the solutions used in these tests varied from about 0.962 to about 1.016 and the viscosity ranged from about 12 to about 27 centipoises. Using these varying proportions, Applicants permitted approximately 3 to 4 minutes for the undried coating to flow downward on the metal strip before exposure to the heat source. The heat source used in this and the following examples was a pair of opposing low-temperature infrared heaters, rated at 750 watts/ft^2, uniformly emitting radiation at approximately 3 microns, with the coated surface or surfaces passing therebetween. (It is understood, however, that this invention is not so restricted in that other heat sources are possible.) The coatings obtained were uniform with thicknesses ranging from about 0.10 to about 0.27 mils.

EXAMPLE 2

Applicants again used a fish glue-water-isopropanol formulation and again achieved satisfactory results. In this particular series of tests, however, the proportions of the solution's components were kept constant and the flow period altered. With a formulation calling for essentially 24% by weight of fish glue, about 41% water, about 33% isopropanol, and ammonium dichromate as a sensitizer added in substantially the same proportions as Example 1, it was determined that altering the withdrawal speed also altered the coating thicknesses obtained. The end result was greater values for the coating thicknesses as the withdrawal speed was increased. The time periods for flow used varied from approximately 2 to 11 minutes with uniform coatings obtained in all cases and ranging from 0.09 to 0.34 mils. The specific gravity for the solution used was approximately 0.982 and the viscosity about 22 centipoises.

EXAMPLE 3

In this series of tests, ethanol was used instead of isopropanol as the alcohol additive and ranged from about 19 to 33% of the solution, fish glue ranged from about 15% to about 29%, water ranged from about 40 to 56%, and ammonium dichromate was added in the same ratio as Examples 1 and 2. The specific gravities of the solutions ranged from about 0.950 to 1.000 and the viscosities varied from about 14 to 24 centipoises. While altering the afore-mentioned formulations within the ranges as listed, Applicants varied the time period for the downward flow from approximately 2 to 3.5 minutes. Again the end result was uniform coatings in all tests with the thicknesses varying from about 0.10 to 0.20 mils.

From the above three examples, it has been determined, therefore, that several fish glue-water-alcohol formulations are acceptable. Compiling the overall ranges which resulted in uniform coatings to the strip, it is determined that aqueous solutions of photosensitive material consisting essentially of fish glue or other type photoresist having substantially similar properties and ranging from about 15 to 29% by weight of solution, water ranging from about 40 to 62% by weight of solution, isopropanol, ethanol, or similar alcohol ranging from about 16 to 33% by weight of solution, and ammonium dichromate or similar type photosensitizer added at a ratio of between 80 and 130 grams per liter of fish glue achieves the uniform coatings desired when utilized with the previously described method. Although isopropanol and ethanol were preferred in the method described herein, the invention is not so restricted as basically any alcohol having the formula $C_nH_{2n+1}OH$ wherein n is an integer having a value of from 1 to 3 is suitable.

Accordingly, while formulations within the ranges described resulted in several successful uniform coatings, on some occasions results were not so favorable. For example, it was determined that by increasing the water content in Example 1 above the prescribed range, non-uniform coatings resulted. This is believed primarily due to the fact that adding water in turn reduced the amount of alcohol additive present which upset the balance between the viscosity and the evaporation rate. When the viscosity readings for these solutions reached approximately 30 centipoises, non-uniform coatings also resulted.

EXAMPLE 4

Alcohol additives were eliminated from the formulations used in this series of tests and simple fish glue-water solutions were employed. With fish glue ranging from about 20 to 28% by weight of solution, water ranging from about 68 to 79% and ammonium dichromate used as a photosensitizer and mixed at a ratio of substantially between 80 and 130 grams per liter of fish glue, several uniform coatings were obtained. Using withdrawal speeds of between 20 and 30 inches per minute and permitting downward flow for time periods between about 2.5 and 5.0 minutes before the strip passed between the heaters, coatings were obtained having thicknesses ranging between about 0.09 and 0.21 mils. The solutions as used had specific gravities ranging between about 1.030 and 1.040 and viscosity values between about 3.0 and 8.0 centipoises.

As mentioned, Applicants obtained several uniform coatings employing the solutions described. However, once again non-uniform coatings resulted when some ranges of the values listed were exceeded. For example, when the withdrawal speeds were reduced to approximately 13 inches per minute, thereby allowing a downward flow period of about 6.5 minutes, irregularities resulted.

From the data obtained in the first three examples, it has been determined that the coating thickness for solutions using alcohol additives can be predetermined by using a modified withdrawal equation:

$$\text{Thickness} = KV\,[m\,(S/P)]^{2/3}$$

wherein K is an experimentally determined constant and

$$V = \frac{\text{Volume of Photosensitive material}}{\text{Volume of Photosensitive material} + \text{Volume of Alcohol} + \text{Volume of } H_2O}$$

m = Viscosity in centipoises,
S = Withdrawal speed, cm/sec, and
P = Specific gravity.

While Applicants prefer using commercially available fish glue in the solutions described, other photoresist solutions (polyvinyl alcohol resists for example) could easily be substituted. Furthermore, the time period stated for allowing downward flow are dependent on two factors; the rate of withdrawal and the height of the heaters for drying the coating. It is obvious, therefore, that various modifications to this date could be made. For example, it may be desirable to raise the elevation of the heater assemblies. To compensate for this, the corresponding speeds of withdrawal would be increased.

While there have been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. In a method for applying a substantially uniform coating of an aqueous solution of a photosensitive material to at least one surface of a substantially vertically moving metallic strip for being later subjected to a photoetching process wherein said method comprises withdrawing said metallic strip in a substantially vertical direction from said aqueous solution of photosensitivee material within a container adapted for containing said material and thereafter exposing said material on said surface to a preestablished heat source whereby said material is dried, the improvement comprising:

providing an aqueous solution of a photosensitive material selected from the group consisting of aqueous solutions of photosensitive materials having a specific gravity within the range of from about 0.950 to about 1.016 and a viscosity within the range of from about 12.0 to about 28.0 centipoises and aqueous solutions of photosensitive materials having a specific graivty within the range of from about 1.030 to about 1.040 and a viscosity within the range of from about 3.0 to about 8.0 centiposies; and

withdrawing said metallic strip from said aqueous solution at a rate within the range of from about 8 inches per minute to about 50 inches per minute to provide a predetermined time period within the range of from about 1 minute to about 11 minutes immediately after said withdrawing of said strip from said solution and prior to said exposing of said strip to said heat source whereby said photosensitive material on said surface of said strip is permitted to flow in a substantially downward direction in such a manner so as to achieve uniformity of thickness.

2. The method according to claim **1** wherein said aqueous solution of photosensitive material consists essentially of fish glue ranging from about 20 to 28% by weight of solution, water ranging from about 68 to 79% by weight of solution, and ammonium dichromate added to said aqueous solution at a ratio of substantially between 80 and 130 grams per liter of fish glue.

3. A method according to claim **1** wherein said aqueous solution of photosensitive material consists essentially of fish glue ranging from about 15 to 29% by weight of solution, water ranging from about 40 to 62% by weight of solution, and alcohol ranging from about 16 to 33% by weight of solution and having the formula $C_nH_{2n+1}OH$ wherein n is an integer having a value from 1 to 3, and ammonium dichromate added to said aqueous solution at a ratio of substantially between 80 and 130 grams per liter of fish glue.

4. The method according to claim **3** wherein said alcohol ranging from about 16 to 33% by weight of solution is isopropanol.

5. The method according to claim **3** wherein said alcohol ranging from about 16 to 33% by weight of solution is ethanol.

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