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3,740,249

**SOLVENT FIXING PROCESS**

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6 Claims

**ABSTRACT OF THE DISCLOSURE**

A process for fixing toner images with a solvent which comprises contacting a film of a solvent formed on the surface of a grounded conductive roller with the front surface of a support having thereon toner images while applying to the back side of the support a corona discharge of a polarity opposite to the charge of the toner images to thereby fix the toner images on the support, said solvent being capable of fixing said toner image and being a non-conductive and non-polar liquid.

**FIELD OF THE INVENTION**

The present invention relates to a novel process of fixing a toner image onto the surface of a support and more particularly, the invention relates to a process of fixing a toner image formed loosely on a xerographic plate, an electrostatic recording paper or on a transfer sheet electrostatically by using a solvent.

**BACKGROUND OF THE INVENTION**

Hitherto, a toner image formed on a support was fixed in electrophotography by one of the following two methods. One method is the use of heat and the second method is the use of solvent.

The first method is unacceptable because of faults such that the power consumed in the fixing by heating is great and there is a danger of fire and the practice of the continuous heating gives harmful influences on the photoconductive layer. In spite of such faults, the fixing method by heating has generally been adopted more favorably than the fixing method by solvent because the solvent fixing method has many faults such that in the so-called solvent-vapor fixing method of condensing the vapor of solvent on the surface bearing thereon a toner image, there is the necessity of a long period of time in the condensation of the solvent vapor, which makes it difficult to speed up the fixing and makes the control and maintenance of vapor difficult. The solvent fixing method has also faults, such that in the method of conducting the solvent fixing by contacting a back surface of the toner image-bearing sheet directly to a metallic roller rotated in a solvent bath with a controlled speed the whole sheet is impregnated with the solvent from the back side thereof, which requires a large quantity of solvent and the sheet is withdrawn from the fixing system in a wet state, which requires an additional drying step.

Therefore, an object of this invention is to provide a novel process of fixing a toner image formed on a support with a solvent with a considerable reduction in consumption and release of solvent as compared with conventional solvent fixing methods. In the specification of this invention, the term "support" means a photosensitive paper or a web sheet of electrostatic recording paper each having a toner image thereon or a web sheet to which a toner image formed on a photosensitive plate has been transferred.

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**BRIEF DESCRIPTION OF THE DRAWINGS**

Now, the principle of this invention will be explained by referring to the drawings, in which:

FIG. 1 is a cross-sectional view showing the typical mechanism of the process of this invention; and

FIG. 2 is a cross-sectional view showing a modification of the process of this invention.

**DETAILED DESCRIPTION OF THE INVENTION**

In FIG. 1, a conductive roller 1 which has been grounded, is rotated by means of a motor (not shown). A solvent 2 placed in a solvent tank 3 is a solvent capable of directly fusing a toner image, a solvent containing a binder, or a solvent containing a plasticizer. That is to say, a liquid used in a conventional fixing method of toner images by solvent, may be used in this invention. The solvent is restricted in electric conductivity to some extent by the reasons shown below. A roller 4 is immersed partially in the solvent and supplies the solvent onto a roller 5 in an amount controlled by a control blade 6. The roller 5 transfers the solvent thus supplied onto the surface of the conductive roller 1 to form a thin film of the solvent on the conductive roller 1. Adjacent to the roller 1 is disposed a cleaner 7 for cleaning away the toner offset on the roller 1. A support having formed thereon toner image 9, is supplied to the solvent fixing system and withdrawn therefrom with fixed toner images 10 by solvent. Under the roller 1 is disposed a corona discharging device 11.

By the mechanism mentioned above, a solvent is supplied from the solvent tank 3 in a suitably controlled amount and the film of the solvent is formed on the surface of the roller 1. The conductive roller 1 is contacted with the surface of the sheet 8 bearing the toner images via corona discharging. The polarity of the corona discharging is so selected that it is opposite to the charge of the toner images 9 formed electrophotographically on the support. By this process, the toner images are brought into contact with the solvent film. Accordingly, the toner images are fixed with a smaller amount of solvent than that in the conventional method and because the amount of the solvent required for the fixing of toner images is less, the support having the fixed toner image withdrawn from the roller 1 is in an almost dry state and hence, requires almost no drying step.

Also by utilizing corona discharging, the sheet 8 is closely brought into contact with the solvent film on the conductive roller 1 to provide uniform fixing and additionally, because the polarity of the corona discharging is opposite to the charge of the toner image, the toner images are attracted strongly to the support by the electrostatic attraction forces to reduce the offset of the toner onto the roller 1 and also thereby reduces the disturbance of the toner images by solvent. As will be understood from the aforesaid mechanism, the evaporation of the solvent at the stoppage of the above fixing system is prevented by stopping the rotation of the roller 4 and closing the solvent tank 3.

Another embodiment of this invention is shown in FIG. 2. By this embodiment, the solvent is supplied to the conductive roller 12 by means of a solvent supplying material 20, such as felt in place of the roller 5 in FIG. 1. That is to say, the solvent supplied to the solvent supply material 20 by means of a rotary roller 15 from a solvent tank, is carried onto the conductive roller 12 by a capillary phenomena to form a thin film of the solvent on the surface of the conductive roller 12.

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## METHOD OF UNIFORMLY COATING A TUBULAR LAMP ENVELOPE WITH PHOSPHOR

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7 Claims

### ABSTRACT OF THE DISCLOSURE

The phosphor paint is flushed through the vertically-positioned envelope and the vaporized solvent is removed from the envelope in such a manner that setting and drying of the coating is accomplished at a rate which deposits a layer of phosphor particles on the inner surface of the envelope that is more uniform than that achieved with conventional coating methods. In the case of a water-base phosphor paint, removal of the water vapor is achieved by passing heated air (approximately 155° F.) downwardly through the coated envelope and varying the velocity of the air flow (within a range of 250 to 650 feet per minute) during the drying operation.

With phosphor paints having an organic solvent (xylene or butyl acetate), the solvent vapors are first flushed out with air through the top of the coated envelope by closing the lower end of the envelope, the injection of air is then stopped and the lower end of the envelope is opened to allow the heavier-than-air solvent vapors to flow out of the envelope through its lower end, and air at a low velocity (150 to 200 feet per minute) is then passed through the envelope to complete the drying cycle.

The coated bulbs in each case are lehrd in air at a temperature of from about 1200° to 1250° F. for about 2 minutes to volatilize and remove the organic binder from the phosphor layer.

### CROSS-REFERENCES TO RELATED APPLICATIONS

The subject matter of the present application is related to that disclosed in copending application Ser. No. 781,515, entitled, "Well Dispersed Water Vehicle Coating Suspension and Method for Preparing Same," filed Dec. 5, 1968, by the same inventor, now Pat. No. 3,585,207; and application Ser. No. 808,801, entitled, "Fluorescent Lamp Having TiO<sub>2</sub> Containing Glass Envelope and Reduced Phosphor Weight," filed concurrently with the present application by Harry H. Haft and the present invention, now Pat. No. 3,581,139. Both of the aforesaid applications are owned by the assignee of the present application.

### BACKGROUND OF THE INVENTION

#### Field of the invention

The present invention relates to electric lamps and has particular reference to a method of coating the vitreous tubular envelope of a fluorescent lamp with a uniform layer of phosphor particles.

#### Description of the prior art

The thickness of the phosphor coating deposited on the inner surface of fluorescent lamps is quite critical since it plays an important role with regard to lamp quality and manufacturing costs. If the phosphor coating is too heavy or thick it will absorb the light rays produced by the phosphor and thus act as a filter that not only decreases the light output of the lamp but increases its manufacturing cost. A phosphor coating which is too thin allows ultraviolet radiations generated by the discharge to pass through the phosphor coating and be absorbed by the glass. This is undesirable since such

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absorbed ultraviolet radiation is lost and produces no visible light. In addition, when the envelope is subjected to ultraviolet radiations it gradually darkens due to the "solarization" effect of the impinging ultraviolet radiation and a chemical reaction which occurs at the phosphor-glass interface and involves the mercury or other materials contained by the lamp.

Thus, the optical thickness of the phosphor coating in a fluorescent lamp is a compromise between (a) preventing ultraviolet radiation from striking the glass envelope and (b) absorbing visible light which is produced by the phosphor particles.

According to present practice fluorescent lamp bulbs are coated with phosphor by flushing the bulbs with a slurry or paint consisting of phosphor particles which are dispersed in a solution of an organic polymer dissolved in either an organic solvent or water. Heated air is then passed down through the vertically held bulbs at a uniform velocity to dry the coating of phosphor paint, thus depositing a layer of phosphor particles that are held in place on the bulb surface by the organic polymer which serves as a binder. The bulbs are then baked or lehrd in air at a temperature sufficient to completely "burn out" or volatilize the organic binder so that only the finely-divided phosphor particles remain on the surface of the envelope. The thickness of the phosphor layer is controlled by adjusting the viscosity of the phosphor paint, the concentration of the phosphor in the coating formulation or paint, and by properly selecting the temperature and uniform velocity of the air which is passed through the envelope and thus determines the rate at which the phosphor paint dries.

The above described conventional coating process produces a phosphor coating having a thickness which varies along the length of the envelope. The process is such that the phosphor coating is thin at the end of the envelope which was uppermost during the flushing and drying operations, and the coating thickness increases gradually toward the lower end of the envelope. As a result, the phosphor coating is thinner than desired at one end of the envelope and thicker than desired at the other end. When made into fluorescent lamps, such prior art phosphor-coated bulbs absorb a large amount of visible light at the "thick" coated end and do not efficiently utilize the ultraviolet radiation at the "thin" coated end. In addition, the thinly coated end of the bulb progressively darkens as the lamp is operated due to the solarization effect of the impinging ultraviolet radiation and the formation of discoloring deposits on the inner surface of the bulb.

### SUMMARY OF THE INVENTION

It is accordingly the general object of the present invention to provide a practical and economical method for coating the inner surface of a tubular lamp envelope with a phosphor layer that is of substantially uniform thickness from one end of the envelope to the other.

Another and more specific object is the provision of a method for depositing a uniform layer of phosphor particles on the inner surface of a fluorescent lamp envelope and controlling the coating thickness so that lamps made with such envelopes will exhibit maximum light output and good lumen maintenance with a minimum amount of phosphor.

The foregoing objectives and other advantages are achieved in accordance with the present invention by controlling the rate at which solvent vapors are removed from the coated bulb during the drying operation. In general, the vapors are removed at a rate such that the phosphor paint is quickly dried at the upper end of the envelope (before too much drainage and thinning-out occurs) and drying along the remainder of the envelope

These objects are accomplished in one aspect of the invention by the provision of a cathodoluminescent material which has thereon an outer layer of chemically combined fluoride ion that is non-luminescent and inert relative to the dichromate ion. The fluoride ion is applied to the phosphor particle by bathing the phosphor in an acidic fluoride solution and then subsequently decanting the solution, washing, filtering and then drying the phosphor.

#### 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.

Referring now to the invention with greater particularity, a luminescent material is provided with a substantially uniform outer layer of inert, non-luminescent chemically combined fluoride ion for the prevention of deleterious reactions with the dichromate ion which will be present in a slurry formulation. The fluoride ion coating is particularly useful when utilized with a luminescent material which comprises at least one rare earth oxide host selected from the group consisting essentially of yttrium oxide, gadolinium oxide and yttrium-gadolinium oxide. The host compound may be activated by at least one of the lanthanide series of elements. In particular, the activator may be selected from the group consisting of europium, samarium, and praseodymium.

It has been found that a luminescent material having such a chemically combined outer layer of fluoride ion is substantially impervious to the chromate ion reaction and has an increased slurry life of up to 160 hrs. This is in contrast to an untreated rare earth oxide host phosphor which will not make a screen after aging as little as twenty-four hours in a slurry.

The phosphor material has the fluoride ion applied thereto by adding to a greater than .03 molar fluoride bath, in an aqueous acidic solution, about 400 to 500 grams of the phosphor per liter of solution. An ideal molar concentration is .05; however, other higher molar concentrations; e.g. .10, may be utilized. A suitable acidic fluoride-containing compound is ammonium bifluoride ( $\text{NH}_4\text{F}\cdot\text{HF}$ ); however, other water-soluble acidic fluorides may be used if desired.

After the phosphor has been added to the solution, the solution is agitated for about 20-30 minutes. Thereafter the acidic solution is decanted, the phosphor is washed, for example in water, and then filtered and dried. The drying step must be carried out at a temperature less than 200° C. to avoid disruption of the fluoride coating. An

optimum temperature range has been found to be approximately 125° C. The time of the drying operation is not critical and will vary in accordance with the amount of phosphor being dried.

Cathodoluminescent screens made by the slurry method and utilizing a phosphor of the type described by this invention show virtually no loss in efficiency or light output when operated with a screen potential of 24-25 kv. The phosphor exhibits excellent adherence qualities with little tendency to form pickouts or other deleterious effects on the screen.

Thus there has been provided by this invention luminescent materials having enhanced adhesive properties particularly when used in the formation of cathodoluminescent screens. Furthermore, the invention is particularly applicable to rare earth oxide host phosphors. Further, there has been provided a simple and efficient and economical method of making these phosphors.

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. A luminescent material consisting essentially of at least one rare earth oxide host selected from the group consisting essentially of yttrium oxide, gadolinium oxide and yttrium-gadolinium oxide, said host compound being activated by at least one of the group consisting of the lanthanide series of elements and said material having a non-luminescent, inert layer of chemically combined fluoride ion only on the outer surface thereof, said layer being applied after said luminescent material is fabricated.

2. The luminescent material of claim 1 wherein said activator is selected from the group consisting of europium, samarium, and praseodymium.

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The coated bulb is then baked or lehrd in air at a temperature of from about 1200° to 1250° F. for from 1 to 2 minutes to volatilize the organic binder (the polyacrylic acid in the aforementioned formulation), thereby completing the phosphor coating operation. The resulting phosphor coating 13 has an optical density of about 28.

The thickness of the finished phosphor coating 13 can be varied by properly adjusting the viscosity of the phosphor paint or suspension. As an example, the viscosity can vary from about 50 to 150 centipoises.

The improvement in the uniformity of the phosphor coating 13 achieved by the present invention compared to conventionally coated bulbs is graphically illustrated in FIG. 4 wherein the optical densities of the respective phosphor coatings are plotted against the distance in inches from the thin end of T12 envelopes that have been made into 4-foot 40-watt lamps. Curve A represents the conventionally coated envelope and curve B the envelope which has been coated in accordance with the above described method. The optical density is a measure of the phosphor thickness and is determined by passing a light beam of predetermined intensity through a portion of the coated lamp envelope perpendicular to its longitudinal axis. The light passing through the lamp envelope strikes a photocell that is disposed a fixed distance (1½ inches) from the bulb axis and the opposite side of the envelope and is connected to a microammeter. The reading registered on the microammeter is the value which is plotted along the ordinate of the graph in FIG. 4. These readings thus provide a measure of the phosphor coating thickness, thin coatings giving a higher reading and heavy coatings a low reading.

As will be noted in FIG. 4, the conventionally coated envelope (curve A) had an optical density of 35 at its thin end and a density of 20 at its heavy end (a spread of 15 units). In contrast, the envelope coated in accordance with the present invention (curve B) had an optical density of only 32 at its thin end and slightly more than 26 at its heavy end (a spread of less than 6 units). In addition, attention is called to the fact that the coating thickness (optical density) of the envelope processed in accordance with the invention remained at a substantially constant value (density of 28) along the central portion of the envelope beginning at 6 inches from its thin end to a point about 3 inches from its opposite end. In contrast, curve A shows that the conventionally coated lamp had a phosphor coating whose thickness varied from one extreme to the other along the entire length of the lamp envelope.

#### ORGANIC-BASE PHOSPHOR COATING SYSTEM

The invention is not limited to water-base phosphor paints but can also be employed in conjunction with a coating system that utilizes an organic solvent, such as xylene or butyl acetate, and an organic binder such as ethylcellulose or nitrocellulose. A suitable formulation using xylene as the solvent is set forth below in Table II.

TABLE II

| Constituent                | Amount (grams) | Percent by weight |
|----------------------------|----------------|-------------------|
| Butanol.....               | 21.5           | 2.6               |
| Xylene.....                | 430.0          | 51.2              |
| Ethylcellulose.....        | 13.5           | 1.6               |
| Calcium halophosphate..... | 375.0          | 44.6              |
| Phosphor.....              | 840.0          | 100.0             |

The resulting organic-base phosphor paint has a viscosity of about 95 centipoises and produces a coating having an optical density of about 29 when applied in the manner described below.

Since the vapors produced by such organic solvents are heavier than air, it is necessary to modify the coating process to remove such vapors in a manner such that the phosphor coating will set and dry at a rate that the coating will be substantially uniform in thickness from one

end of the bulb to the other. It has been found that the desired uniform coating thickness can be achieved with phosphor paints of this type by temporarily closing off the lower end of the vertically positioned envelope, as by means of a suitable cap, after the phosphor paint is flushed through the envelope 12. Air is then introduced into the upper end of the bulb at a velocity of about 500 feet per minute, the air being heated to a temperature of about 70° to 90° F. This increases the rate of drying at the upper end of the envelope 12 and permits the air to circulate within the upper end of the vertically-held bulb and flush out the accumulated vapors released by the organic solvent. After about 2 minutes the cap is removed from the lower end of the envelope and the introduction of the heated air is stopped to allow the heavy vapors to flow freely out of the lower end of the envelope. After about 5 minutes, air at a temperature of about 70° to 90° F. is passed downwardly through the envelope at a velocity of from 100 to 150 feet per minute to set and dry the coating at the extreme lower end of the envelope. As will be appreciated by those skilled in the art, the temperature and velocity of the air flow through the envelope will vary depending upon the viscosity of the phosphor paint and the specific phosphor coating thickness which is desired.

After the coating of phosphor paint has been completely dried, the envelope 12 is again baked or lehrd in the same manner as described previously to volatilize and remove the ethylcellulose or nitrocellulose binder from the phosphor layer. The envelope is then ready for the next step in the lamp-manufacturing operation.

It will be appreciated from the foregoing that the objects of the invention have been achieved in that a very economical and convenient method for uniformly coating a fluorescent lamp envelope with finely-divided phosphor particles has been provided. The improved method is particularly advantageous in that it provides a practical process for forming the extremely thin phosphor coatings of the type required to drastically reduce the amount of phosphor required per lamp in accordance with the teachings of the aforementioned concurrently filed Haft et al. application Ser. No. 808,801. Another valuable feature of the invention is that the method can be readily adapted to high-speed automatic coating machine now in use.

While several embodiments have been illustrated and described, it will be appreciated that various modifications in the phosphor paint formulations and drying schedules can be made without departing from the spirit and scope of the invention.

I claim as my invention:

1. The method of coating the inner surface of a tubular lamp envelope with a substantially uniform layer of finely-divided phosphor particles, which method comprises the following sequence of steps:

suspending the phosphor particles in a solution comprising a vaporizable solvent and a temporary organic binder to form a phosphor paint of predetermined viscosity, said binder being a material that volatilizes when heated to a predetermined temperature,

flushing the phosphor paint through said envelope while the latter is held in a vertical position,

immediately introducing into the upper end of said vertically-held envelope heated air at a predetermined velocity and, subsequently, at a lower velocity to thereby remove the vapors produced within said envelope by said solvent at a rate such that setting and drying of the deposited coating of phosphor paint is accelerated at the top of the envelope and then proceeds at a slower rate to the lower end of the envelope such that the resulting dried coating of phosphor paint is substantially uniform along the length of the envelope, and then

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lehring the coated envelope for a time and at a temperature sufficient to volatilize and remove the residual organic binder from the deposited layer of phosphor particles.

2. The method of claim 1 wherein:

the vaporizable solvent constituent of the phosphor paint comprises an organic material which produces vapor that is heavier than air,

the lower end of the envelope is closed during the initial phase of the drying operation and the velocity of the heated air initially introduced into the upper end of the envelope is such that the heated air circulates through the top portion of the envelope and thus flushes the accumulated solvent vapors thereat out of the envelope through the upper end thereof,

the introduction of heated air into the upper end of the envelope is then terminated and the lower end of the envelope is opened to permit the solvent vapors to flow freely out of the envelope through the lower end thereof, and

heated air at said lower velocity is then passed downwardly through the opened envelope to complete the drying of the deposited coating of phosphor paint.

3. The method of claim 2 wherein said organic solvent is a material selected from the group consisting of xylene and butyl acetate.

4. The method of claim 2 wherein:

said organic solvent is xylene and said volatilizable organic binder is ethylcellulose,

said phosphor paint has a viscosity of from about 50 to 150 centipoises,

the air initially introduced into the envelope while the lower end thereof is closed is heated to a temperature of from about 70° to 90° F. and has a velocity of about 500 feet per minute, and

the air passed through the envelope after the lower end thereof is opened to the atmosphere is heated to a temperature of from about 70° to 90° F. and has a velocity of from 100 to 150 feet per minute.

5. The method of claim 1 wherein:

the vaporizable solvent constituent of the phosphor paint comprises water and the volatilizable organic binder constituent is a material which is water soluble, the heated air is passed downwardly through the vertically-held envelope at an initial velocity such that the setting and drying of the coating of phosphor paint deposited on the inner surface of the envelope com-

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mences at the upper end of said envelope while the phosphor paint is still draining from the remainder of the envelope,

the velocity of the heated air passed through said envelope is then decreased to said lower velocity and maintained at such velocity until the coating of phosphor paint has been set along substantially the entire length of the envelope, and

the passage of heated air through said envelope is continued at a velocity greater than said lower velocity until the coating of phosphor paint has completely dried.

6. The method of claim 5 wherein:

the volatilizable organic binder constituent of the phosphor paint comprises polyacrylic acid and the viscosity of the phosphor paint is from about 50 to 150 centipoises,

the air which is passed through the envelope is heated to a temperature of approximately 155° F.,

the air velocity is initially about 650 feet per minute and is maintained at such velocity for approximately 2 minutes,

the velocity of the heated air is then decreased to about 250 feet per minute and is maintained at such velocity for approximately 8 minutes, and

the velocity of the heated air is then increased to about 650 feet per minute and is maintained at such velocity for approximately 5 minutes.

7. The method of claim 6 wherein the coated envelope is lehered at a temperature of about 1200° F. for approximately 2 minutes to volatilize and remove the polyacrylic acid from the phosphor layer.

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