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COLOR CATHODE RAY TUBE SCREENS

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FIG. 1

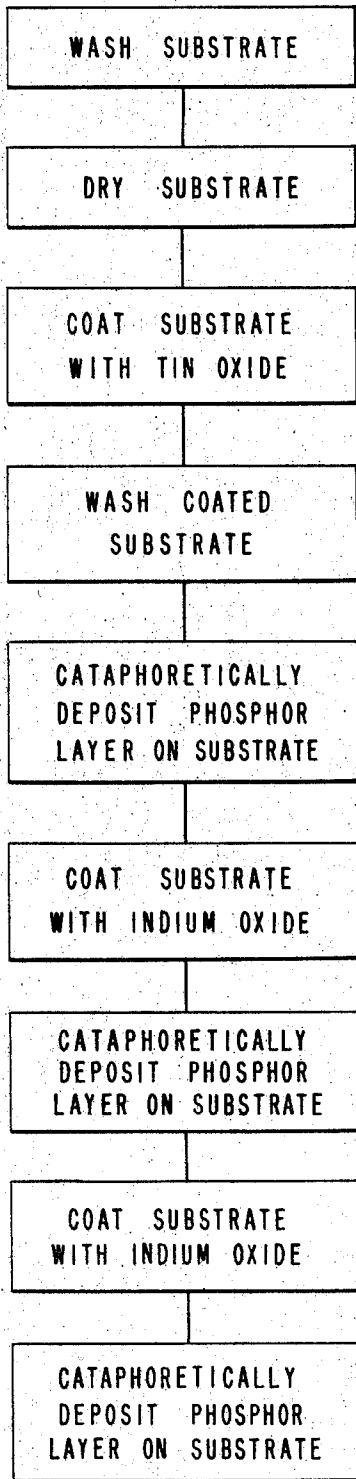


FIG. 2

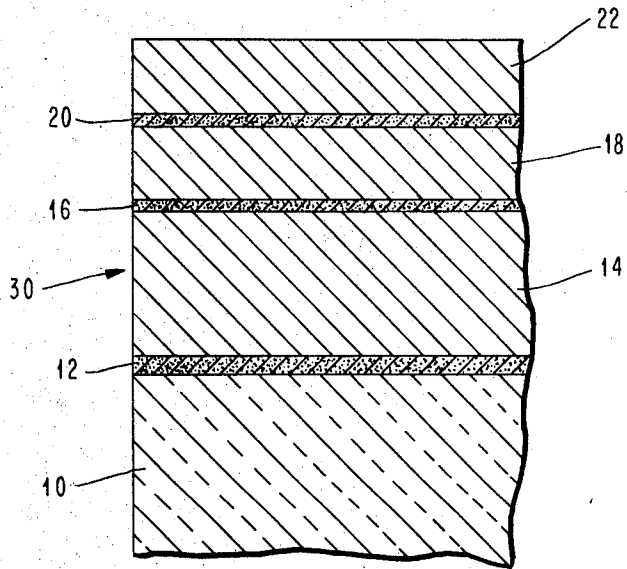
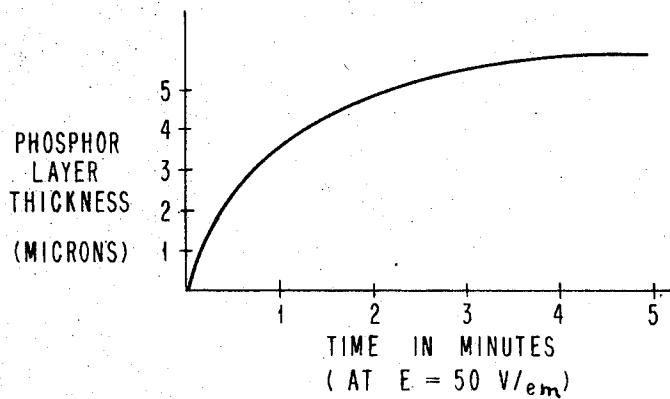


FIG. 3



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COLOR CATHODE RAY TUBE SCREENS

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8 Claims

ABSTRACT OF THE DISCLOSURE

A luminescent color cathode ray tube screen is produced by cataphoretically depositing two or more phosphor layers onto intervening transparent electrically conductive layers on a transparent base. Accurate phosphor layer thickness control is enabled by controlling the cataphoretic deposition parameters, such as field strength, time and solution concentration.

BACKGROUND OF THE INVENTION

This invention relates generally to the production of luminescent screens which are useful, for example, in producing cathode ray tubes (CRT) for the production of color images. More specifically, the invention relates to improved methods for producing multiple phosphor layers on CRT screens.

It is recognized that color CRT displays may be most effectively produced by the use of multiple phosphor layers on a substrate or screen. The multiple layer color screen approach has several important advantages over the previous stripe phosphor screen or shadow mask or dot screens. For example, multiple layer color screens have better resolution, contrast and brightness, and enable the use of single electron gun systems.

There are several conventional techniques for producing multiple phosphor layer color CRT screens. However, if it is desired to produce a multiple phosphor layer color CRT screen that is suitable for high density applications such as in computer-controlled generation of numerics and vectors, the conventional techniques are unsatisfactory.

One present technique of producing multiple phosphor layer color CRT screens is known to the art as gravity or liquid settling. In this approach, phosphor silicate is permitted to precipitate through an electrolytic cushion onto a screen by gravity. Another conventional method of applying phosphor coatings to CRT screens is by the well known vacuum evaporation technique. Other known techniques include spraying and vapor deposition. Each of these above-mentioned techniques has several deficiencies that the present invention is aimed at overcoming.

One known deficiency of the multilayer gravity or liquid-settled screen approach is that the phosphor layers are characterized by excessive graininess and lack uniformity in thickness. This results in poor image resolution, low contrast gradient and poor color quality. Gravity or liquid-settled multiple layer color screens also do not have adequate luminescence for viewing in high ambient lighting, because the intrinsic efficiency of the phosphor has normally been reduced by severe comminution in an attempt to attain high resolution. Further, these thick granular multiple layer screens require high acceleration voltages for excitation, and consequently, beam deflection sensitivity is low. Moreover, due to non-uniformity of the phosphor layers, normally less than one-half the screen surface is available for displaying high density graphics or the like.

A problem with the evaporation or vapor-phase-reacted phosphor screens is that they suffer from a lack of lumi-

nescent efficiency, and image contrast is low in high ambient illumination conditions. Further, the thermal processing that is necessary to produce these type screens limit the substrate materials to quartz, and the high temperature necessary for activation enhances the interaction and bleeding of the phosphor layers. The spraying technique suffers from similar deficiencies. Also, in each known prior art technique, as described above, there is great difficulty in obtaining precisely controlled thickness of the various phosphor layers.

Accordingly, it is an object of the present invention to provide an improved process for producing multiple layer luminescent CRT screens suitable for use with single electron gun systems that substantially overcomes the disadvantages of the prior art techniques or processes.

More specifically, it is an object of the present invention to provide an improved process for producing multiple phosphor layers on CRT screens that are characterized by high resolution, good contrast and generally good image quality and the CRT screens produced thereby.

It is another object of the present invention to provide improved methods of applying multiple layers of phosphors on CRT screens at precisely controlled thicknesses.

SUMMARY OF THE INVENTION

In accordance with the preferred embodiment of the invention, a thin transparent conductive coating of a material such as tin oxide is applied to a transparent glass screen that has been previously cleaned. The tin oxide is preferably applied by chemical deposition onto a heated screen from a solution of tin chloride and antimony-trichloride in a methanol base, and in a water vapor atmosphere. This conductive coating provides an electrode for cataphoretic deposition. A first phosphor layer, having a thickness of approximately four microns is cataphoretically deposited over the thin transparent conductive coating, with the thickness of the first phosphor layer being controlled to within one micron. Over this first phosphor layer there is applied another thin transparent conductive coating of indium oxide or the like. This second thin transparent conductive coating provides the electrode for another cataphoretically deposited layer of phosphor, having a thickness of approximately two microns, and permits the thickness of the phosphor deposit to be controlled to within one-half micron. Subsequently, an additional thin transparent coating or coatings and cataphoretically deposited layer or layers of phosphor may be applied if desired.

The above invention is extremely useful in producing high quality multiple layer phosphor CRT screens, which are especially useful, for example, in high density graphic display applications. Further, the preferred method enables the production of such screens in large sizes, and the method is relatively simple and inexpensive to practice.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the steps comprising the preferred method of the present invention;

FIG. 2 is an enlarged partial cross section through a CRT screen produced in accordance with the method illustrated in FIG. 1; and

FIG. 3 is a chart showing the variables that may be controlled to employ the method of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment of the present invention is shown in FIG. 1. In accordance with the method of preparing multiple-layer color CRT screens, a transparent glass base or substrate 10 (FIG. 2) is initially provided with a so-called "electronically clean" surface. In the pre-

ferred embodiment, a standard CRT soft-lead glass faceplate was used. In order to render the surface "electronically clean," the screen surface is initially washed with detergent and soaked in chromic acid, flushed with water, soaked in ammonium bifluoride, and rinsed with pure water. The screen is then dried in a clean atmosphere.

The method of applying multiple layers of phosphors on the "electronically clean" glass substrate 10 initially involves coating the screen with a thin transparent conductive coating which, in the preferred embodiment, is tin oxide. The thin transparent conductive coating 12 (FIG. 2) is applied to the screen in the following manner. Initially, a solution of tin chloride and methanol, mixed with 5 percent antimony-trichloride (by weight) is prepared. The solution is chemically deposited on the substrate 10 by heating the substrate, in any convenient way, to approximately 425° C., and spraying the solution thereon in the presence of a water-vapor atmosphere. A chemical deposition of tin oxide is achieved by the chemical interaction of the vapors as explained, for example, in U.S. Pat. No. 2,732,313. The resulting transparent conductive coating 12 comprises tin oxide, which is doped with antimony. The antimony doping serves the purpose of shifting the light transmissivity of the coating from near-infrared to the visible spectrum, and of enhancing the conductivity of the coating. The preferred thickness of coating 12 is approximately 5,000 A., and this thickness is controlled by measuring the resistance during the chemical deposition, in a manner well known to those skilled in the art. In the example, the tin oxide coating 12 has a surface resistance of approximately 30 to 40 ohms per square, and an optical transmissivity of approximately eighty percent. After the tin oxide coating 12 is applied, the screen is washed with detergent and soaked in chromic acid and flushed with water.

In accordance with the preferred embodiment of the present invention, a zinc cadmium sulfide (silver-activated) phosphor layer (commonly known as "P-20") having a thickness of four±one micron is applied by cataphoretic deposition. In this regard, the following suspension is prepared. Elutriated fine particles of the preferred phosphor, approximately one to two microns in diameter are suspended in ethyl alcohol containing five percent water (by weight) and 10⁻⁴ moles per liter of thorium nitrate. Preferably, 3.5 mg. of phosphor per ml. of vehicle is used. The suspension is formed by addition of these ingredients, and agitation for approximately 30 minutes by milling, stirring, or vibration. It is important that the dielectric constant of the vehicle be approximately 30 since this will insure a relatively high mobility of the charged phosphor particles through the vehicle and will permit a low field strength to promote cataphoretic movement of the particles.

A phosphor layer 14, having a green color when activated, is cataphoretically deposited on the screen over the conductive coating 14 by initially placing the above-described suspension in a suitable container (not illustrated) having an electrode placed therein. In the preferred embodiment, the coated substrate 10 is connected to the negative terminal of a D.C. power supply and a platinum electrode is connected to the positive terminal of that supply in order to practice cataphoresis. The platinum electrode is preferably located two centimeters from the tin oxide coating 12, and a field of approximately fifty volts per centimeter is applied across the electrodes. It must be noted at this point, as will be explained more fully hereinafter, that the thickness of the phosphor layer 14 is extremely important to the successful production of a multi-phosphor layer CRT screen. Accordingly, reference should be made to FIG. 3 wherein a curve is presented that illustrates the relationship of the three parameters that effect the control of the thickness of phosphor layer 14 by cataphoretic deposition; i.e., time, field strength and concentration of deposition suspension. It will be observed that for the suspension

noted above, and at a field strength of fifty volts per centimeter, it takes approximately 1.5 minutes to deposit a four micron thick phosphor layer 14 on the coated substrate. For reasons to be explained hereinafter, that the thickness of phosphor layer 14 is preferably between three and five microns.

After the first phosphor layer 14 is cataphoretically deposited over the first thin conductive transparent coating of tin oxide 12, a second transparent conductive coating 16 having a thickness ranging from 400 A. to 500 A. is applied. In the preferred embodiment, the coating 16 is indium oxide, and is applied by vacuum deposition. In this regard, the substrate 10 carrying coating 12 and layer 14 thereon, is located in a vacuum chamber and heated to approximately 350° C. Located in the chamber is an indium filament. In order to provide the necessary water vapor and oxygen for the formation of indium oxide, oxygen and water vapor is gradually bled into the chamber, and simultaneously the indium is evaporated from the filament. The various vapors react in a manner well known to those skilled in the art to form an indium oxide coating or film 16 over the first phosphor layer 14. The process is controlled to deposit a coating or film 16 on the order of 400 A. to 500 A. in thickness, for a reason to be related hereinafter.

It was unexpectedly found that a second phosphor layer 18 can now be deposited onto the substrate 10 over transparent conductive coating 16 at a thickness that may be very carefully controlled by using the coating 16 as an electrode for cataphoretic deposition. In the preferred embodiment, a zinc sulfide silver activated layer 18 (a blue phosphor, commonly known as "P-11" is deposited by cataphoresis as follows. The screen 10, carrying the tin oxide coating 12, green phosphor layer 14 and indium oxide coating 16 is again placed in a container along with a zinc sulfide silver activated phosphor suspension that is prepared in the same manner and has the same concentration as explained above. The phosphor layer 18 is cataphoretically deposited over the second thin conductive coating 16 using an electrode spacing of approximately two centimeters and a field strength of approximately 50 volts per centimeter. The thickness of the blue phosphor layer 18 is carefully controlled to be within the range of one and one-half to two and one-half (or two±one-half) microns.

In the preferred embodiment of the invention, another indium oxide coating 20 is applied over the blue phosphor layer 18 in the same manner as described above in regard to the application of indium oxide coating 16. This coating 20 is also preferably 400 A. to 500 A. in thickness, and provides an electrode for cataphoretic deposition. At this time, a third phosphor layer 22 of yttrium vanadate europium activated (or rare earth red phosphor) is cataphoretically deposited in the same manner as the phosphor layers 14 and 18. The thickness of this third phosphor layer 22 is carefully controlled to within the range of one and one-half to two and one-half (or two±one-half) microns. At this time, and in accordance with the conventional method of producing CRT screens, an ion-burn resistant layer of aluminium may be applied over the third phosphor layer 22, to form a multi-layer color CRT screen 30.

As will be noted from the above description, the overall thickness of the three phosphor layers applied by cataphoretic deposition in accordance with the present invention, is six to ten microns. This thickness is very important since electron penetration is proportional to the square of the applied voltage, and to permit the application of voltage in a useful range (i.e., eighteen kv. or less) the total thickness of the phosphor layers 14, 18 and 22 must be held to ten microns or less. Eighteen kv. is considered the maximum useful voltage in CRT graphic applications due to safety considerations since operators are present, and due also to increased tube life and ease of beam deflection. It was found that the only satisfactory

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method of insuring that the three phosphor layers were held to tolerance was by cataphoretically depositing the phosphor layers over thin transparent conductive coatings in this prescribed manner so as to permit precise thickness control of each layer.

In a multi-layer color CRT screen 30 actually produced in accordance with the method of this invention, the overall thickness of the three phosphor layers was less than ten microns and, as mentioned above, only eighteen kv. or less is necessary to provide electron penetration of the screen. This screen is extremely useful in the display of high density numerics or graphics since the phosphor layers, besides being held to precise thickness tolerance by virtue of the intervening conductive layers acting as electrodes for cataphoretic deposition, are characterized by fine uniform particle size, which leads to high resolution, good contrast and generally good image quality. Furthermore, it is anticipated that a screen 30 produced in this manner will experience infrequent electronic breakdowns due to the relatively low voltage that is required to effectively excite the intervening phosphor layers. Also, the carefully controlled thickness of the various phosphor layers 14, 18 and 22 and the intervening conductive layers leads to good color purity without the necessity of controlling voltage on intervening layers in a manner known to the prior art.

While in the preferred embodiment of the invention as described above, certain suspensions and other parameters were mentioned, it would be apparent to those skilled in the art that certain alternatives may be used to practice the invention. For example, the first thin conductive coating 12 may alternatively be indium oxide, sprayed upon the screen as described above. The solution in such case would consist of indium chloride, methanol and antimony-trichloride. It should be noted, of course, that the surface resistance of an indium oxide coating is approximately 150 to 200 ohms per square, and it would therefore not be as conductive as the tin oxide coating 12.

Certain other alternatives to the formation or application of the first conductive coating 12 include using titanium chloride to form a titanium oxide layer that is thereafter rendered conductive by reduction with zinc sulfide in accordance with the method suggested in U.S. Pat. No. 2,928,975. Still other alternatives to the formation of coating 12 that may occur to those skilled in the art include the vacuum evaporation of indium metal at partial pressure to form a transparent conductive coating of indium oxide; the vacuum evaporation of silver or aluminium metals and the subsequent glow discharge thereof in air to render it transparent; and, the vacuum evaporation of aluminium onto the substrate 10 to a thickness of approximately 1,000 A. In this last case, the aluminium would not be transparent initially, and after the first phosphor layer 14 is cataphoretically deposited, the aluminium must be rendered transparent by oxidation in air or in aqueous ammonium persulphate, or anodization by citric acid. Of course, the premature oxidation or anodization of the aluminium, i.e., before deposition of layer 14 would render it non-conducting, and useless for the cataphoretic deposition of layer 14.

In the formation of the phosphor suspensions, it would be apparent to those skilled in the art that methyl-isobutyl ketone may be used as the vehicle rather than ethyl alcohol. Further, rather than provide 10^{-4} moles per liter of thorium nitrate, which incidentally provides an ionizable metal in suspension, it would be possible to utilize nitric or acetic acid to provide an ionizable salt. However, it was found that the thorium nitrate gives better adhesion than those acids, possibly due to a hydroxide occlusion at the interface between the conductive coating and phosphor layer, and therefore thorium nitrate is preferred.

In the preferred embodiment of the invention, the second transparent coating 16 of indium oxide is applied by vacuum deposition. This method was employed rather than chemical vapor deposition, as used for the first coat-

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ing 12, since known chemical vapor depositions react with phosphor. Thus, while conductive metals such as tin, indium or titanium can be applied by vacuum deposition to provide the second and subsequent conductive coatings, chemical vapor deposition may be only used to provide the first coating; i.e., the coating immediately adjacent the glass substrate 10. Further, aluminium may not be applied by vacuum deposition in the presence of water vapor since this causes the aluminium to oxidize which will render it non-conductive. In this regard, aluminium may be applied by vacuum deposition without the presence of water vapor to provide, for example, the first coating 12, and such a coating rendered transparent after the cataphoretic deposition of the phosphor layer as described above.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that various other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A method of producing a cathode ray tube screen having multiple layers of phosphor excitable by a single electron gun, comprising:
 - a) applying to a glass substrate a thin transparent conductive coating to act as an electrode for cataphoresis;
 - b) cataphoretically depositing from a suspension a layer of phosphor having a thickness ranging from three to five microns over the thin transparent conductive coating;
 - c) applying over the layer of phosphor a second thin transparent conductive coating to act as an electrode for cataphoresis; and
 - d) cataphoretically depositing from another suspension at least another layer of phosphor having a thickness ranging from one and one-half to two and one-half microns over the second thin transparent conductive coating.
2. The method set forth in claim 1, wherein the step of applying to a glass substrate a thin transparent conductive coating includes depositing on the glass substrate a coating selected from the group consisting of tin oxide, indium oxide, conductive titanium oxide, and transparent silver.
3. The method set forth in claim 1, including the step of applying a third thin transparent conductive coating over the another layer of phosphor; and
 - a) cataphoretically depositing from another suspension a third layer of phosphor having a thickness ranging from one and one-half to two and one-half microns over the third thin transparent coating.
4. The method set forth in claim 3 wherein the steps of applying to a glass substrate a thin transparent conductive coating, applying over the layer of phosphor a second thin transparent conductive coating, and applying a third thin transparent coating over the another layer of phosphor each comprises depositing a coating selected from the group consisting of tin oxide, indium oxide, conductive titanium oxide, and transparent silver.
5. A method of producing a cathode ray tube screen having three discrete phosphor layers, comprising:
 - a) applying to a surface of a transparent substrate a coating of tin oxide having a thickness of approximately 5,000 A.;
 - b) cataphoretically depositing over the tin oxide coating a first layer of phosphor ranging from three to five microns in thickness;
 - c) applying over the phosphor layer a coating of indium oxide ranging from 400 A. to 500 A. in thickness;
 - d) cataphoretically depositing over the indium oxide coating a second phosphor layer having a thickness ranging from one and one-half to two and one-half microns;

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applying over the second phosphor layer a second coating of indium oxide ranging from 400 A. to 500 A. in thickness; and cataphoretically depositing over the second coating of indium oxide a third phosphor layer having a thickness ranging one and one-half to two and one-half microns.

6. A transparent color image screen comprising:

a transparent glass base;
a first conductive transparent layer adjacent the transparent glass screen;

a first cataphoretically deposited phosphor layer having a preselected color when excited and having a thickness ranging from three to five microns, the first cataphoretically deposited phosphor layer being adjacent the first conductive layer;

a second conductive transparent layer adjacent the first cataphoretically deposited phosphor layer; and

a second cataphoretically deposited phosphor layer having another preselected color when excited and having a thickness ranging from one and one-half to two and one-half microns, the second cataphoretically deposited phosphor layer being adjacent the second conductive transparent layer.

7. The transparent color image screen of claim 7 in-

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cluding a third transparent conductive layer adjacent the second cataphoretically deposited phosphor layer; and a third cataphoretically deposited phosphor layer adjacent the third conductive transparent layer, said third cataphoretically deposited phosphor layer having a thickness ranging from one and one-half to two and one-half microns.

8. The transparent color image of claim 6 wherein the first conductive transparent layer is approximately 5,000 A. in thickness, wherein the second conductive transparent layer ranges from 400 A. to 500 A. in thickness, and wherein the third conductive transparent layer ranges from 400 A. to 500 A. in thickness.

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U.S. Cl. X.R.

117-215, 33.5