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Phillips

[11] **3,904,502**

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[54] **METHOD OF FABRICATING A COLOR DISPLAY SCREEN EMPLOYING A PLURALITY OF LAYERS OF PHOSPHORS**

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[52] **U.S. Cl.** **204/181;** 313/64
[51] **Int. Cl.²** **C25D 13/04;** C25D 13/12
[58] **Field of Search** 204/181

[56] **References Cited**

UNITED STATES PATENTS

3,314,871	4/1967	Heck et al.	204/181
3,554,889	1/1971	Hyman et al.	204/181

Primary Examiner—Howard S. Williams
Attorney, Agent, or Firm—W. G. Sutcliff

[57] **ABSTRACT**

A method of fabricating a color display screen that produces light of different colors in response to impinging electrons of different energies. The method provides fabrication of a plurality of layers by electrophoresis to provide smooth and even layers with uniform boundaries between the layers. The electrical conducting coating utilized in the electrophoresis process may be removed after the deposition of the layers.

8 Claims, 5 Drawing Figures

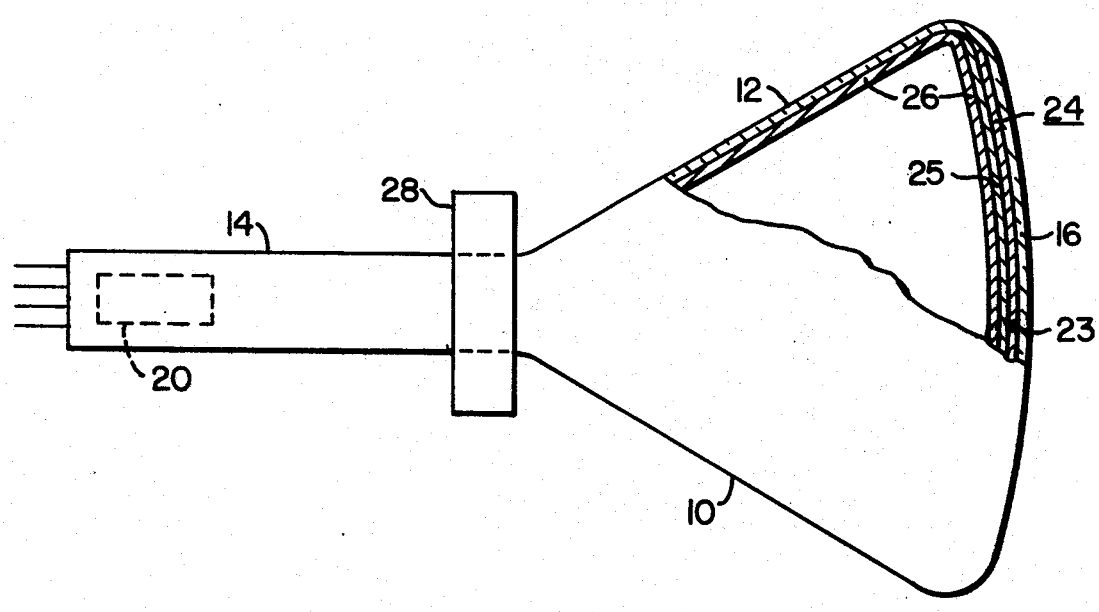


FIG.1

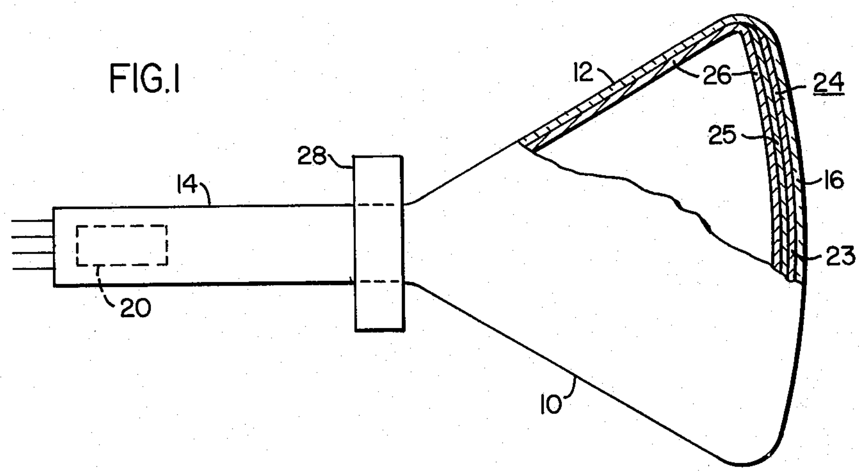


FIG.2

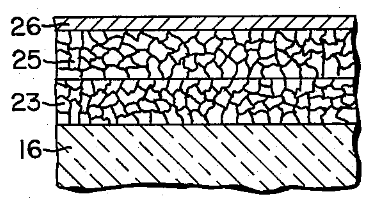


FIG.3

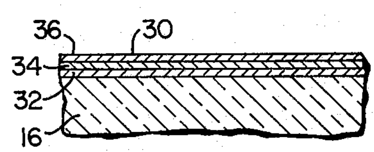


FIG.4

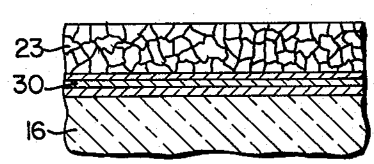
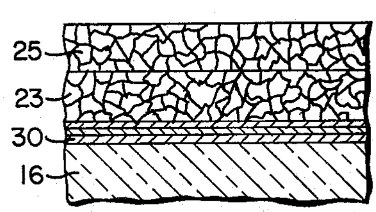


FIG.5



METHOD OF FABRICATING A COLOR DISPLAY SCREEN EMPLOYING A PLURALITY OF LAYERS OF PHOSPHORS

BACKGROUND OF THE INVENTION

This invention is related to the method of fabricating a color display screen and more particularly to such a screen of the type which produces light of different colors in response to impinging electrons of different energies. Most of the state of the art type of devices utilize a two layer voltage dependent screen which consists of a front phosphor screen, an electron barrier layer, and a second phosphor screen. The barrier layer acts as a buffer zone for blocking low voltage electrons thus preventing electron beam excitation of the front screen during the low voltage operation of the tube, while at the same time permitting light from the rear screen to pass through both the buffer layer and the front screen. This barrier layer may be composed of silicon monoxide or magnesium oxide for example. In both of these materials, the barrier layer provides a buffer and a filter between two relatively rough surfaces of the front and rear screen. If the barrier layer were not present, the surfaces of the two screens would intermesh into one another at their interface, thereby preventing good clear separation and purity with respect to the front and rear phosphor screen. A barrier layer such as magnesium oxide will result in considerable light from the rear screen being lost due to the opacity of the layer. In the case of silicon monoxide, the layer must be thin enough to permit passage of high voltage electrons and be free of voids which would permit passage of low voltage electrons. These difficulties found in prior art devices have resulted in some attempts to solve the problem by coating all the phosphor particles with an electron blocking coating; thereby increasing the thickness of this barrier coating on each particle results in the requirement for an additional electron bombardment energy to excite the phosphor.

It is particularly important in some such devices to provide a high resolution. It is known in the art that a single phosphor layer deposited by the electrophoresis technique provides a high resolution type screen. A process for fabricating such an electrophoretic type deposit is disclosed in U.S. Pat. No. 3,525,679 issued Aug. 25, 1970 to the same assignee as this invention.

SUMMARY OF THE INVENTION

A cathode ray display device, and method of producing same, is disclosed which produces light of varying color in response to electron excitation of varying energy. The display screen of the device comprises a plurality of distinct thin phosphor layers. Each phosphor layer comprises a material with a diverse color output from the other phosphor layer. The distinct layers have a very high uniformity of average thickness.

The phosphor layers are successively deposited upon the substrate by an electrophoretic process, which provides the high uniformity of layer thickness, which is the key to high resolution and color discrimination.

BRIEF DESCRIPTION OF THE DRAWING

For a better understanding of the invention, reference may be had to the preferred embodiment, exemplary of the invention, shown in the accompanying drawing, in which:

FIG. 1 shows a partially sectionalized cathode ray tube in connection with which the present invention may be usefully utilized;

FIG. 2 is an enlarged sectional view of a portion of the screen of the tube shown in FIG. 1; and

FIGS. 3 through 5 inclusive are enlarged views, in section, illustrating various steps in the process embodying the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A color television tube is illustrated in FIGS. 1 and 2. The tube includes an envelope **10** having an enlarged flared portion **12**, a neck portion **14** and a faceplate portion **16**. An electron gun **20** is provided within the evacuated envelope and within the neck portion **14** for generating an electron beam which is directed onto the faceplate **16**. The faceplate **16** provides a substantial transparent window to the radiations emitted by a cathodoluminescent screen **24**.

The screen **24** is comprised of a plurality of distinct thin layers of cathodoluminescent phosphors illustrated as layers **23** and **25**. Phosphor layer **23** is deposited on the inner surface of the faceplate portion **16** and is termed the front phosphor layer. The second phosphor layer **25** is deposited on the rear surface of the layer **23**. A thin electrically conductive layer **26** of a suitable material such as aluminum is provided on the inner surface of the luminescent layer **25** for both improving the light output from the screen **24**, as well as preventing ion burn of the material in the layers **23** and **25**. A suitable deflection system **28** may also be provided for deflecting the electron beam across the screen **24**. The front layer **23** may be of any suitable phosphor, which is for example P–1 zinc silicate activated by manganese and emits a green color. The second layer **25** may be a suitable phosphor, which is for example, P–22R, yttrium oxide activated by europium, which emits a red color. Thus, the tube will emit in response to low energy excitation the color of the second layer **25**, and in response to higher energy excitation will emit a combination of the colors from the two layers.

In the manufacture of the screen of the present invention, a glass panel of suitably transmissive glass is first provided with a thin electrical conductive transparent film **30**. The conductive film **30** illustrated in FIG. 3 comprises a plurality of conductive metal layers **32, 34** and **36**, which may be applied by several techniques such as outlined in aforementioned U.S. Pat. No. 3,525,679. It is necessary that it have a resistivity of about 100 ohm centimeter. In one specific process, the glass is first cleaned by a suitable standard procedure such as treating with hydrofluoric acid. The individual conductive layers **32, 34** and **36** can now be deposited on the faceplate. The layers **32, 34** and **36** are by way of example respectively aluminum, gold and indium. The faceplate **16** is then positioned in a vacuum system which is at a pressure of about 10^{-5} Torr. With the faceplate **16** having a diameter of about 5 inches, 5 milligrams of aluminum are positioned within an open crucible at a distance of about 19 inches from the faceplate **16**, and the aluminum is evaporated to provide a layer **32** of a few angstroms in thickness. The aluminum layer **32** is illustrated in FIG. 3 and provides better adherence of the gold layer **34**. After the coating **32** is applied, a crucible containing about 100 milligrams of gold is positioned within the evacuated chamber and about 19 inches from the faceplate **16.** The layer **34** of gold is evaporated onto the layer **32.** The gold layer **34** is also only a few angstroms in thickness, but is thicker than the layer **32.** After the evaporation of the gold layer **34,** a protective coating **36** of a suitable material such as indium is evaporated onto the gold layer **34,** by placing about 3 milligrams of indium in a crucible about 19 inches from the faceplate **16.** The indium layer **36** protects the gold layer **34** and makes it thermally stable. A reading of the transmission of the radiations of wavelength of about 5000 angstroms through the conductive layers **32, 34** and **36** and the faceplate **16** is about 75%. The resistivity of this resulting substrate of layers **32, 34** and **36** is about 100 ohm centimeter, and provides an excellent conductive electrode for the deposition of the luminescent layers **23** and **25.**

The conductively coated faceplate seen in FIG. **3,** is then ready for electrophoretic deposition of the phosphor layers thereon. The faceplate is immersed in a phosphor bath which contains the finely divided zinc silicate front phosphor, in an amount sufficient to provide the desired layer thickness for a given faceplate size. The zinc silicate phosphor particles have an average particle diameter of less than about 1.5 microns. The phosphor bath contains for example about 10 grams of the phosphor, about 200 milligrams of a suitable electrolyte such as thorium nitrate, and about 900 millileters of alcohol. This mixture is elutriated for a given period of time, for example four hours, for the purpose of obtaining the necessary small particle size of phosphor in suspension. The suspension is gently agitated during the deposition of phosphor onto the substrate. The conductive film **30** is connected to a source of potential. The phosphor bath container is typically stainless steel which serves as the anode which is also connected to the source of potential. The electrophoretic deposition is effected in about ten seconds by applying about 150 volts d.c. across the anode and film **30.** The time can be readily varied to vary the phosphor layer thickness, and the article will then be as seen in FIG. **4,** with the front phosphor layer being preferably from about 3 to 5 microns thick.

The faceplate with front phospor layer **23** deposited thereon is thereafter introduced into a second phosphor containing bath to effect electrophoretic deposition of phosphor layer **25** in the same manner as already specified above for front phosphor layer **23.** The other phosphor layer **25** is for example europium activated yttrium oxide having an average particle diameter of less than about 1.5 microns, and the preferred thickness of layer **25** is from about 5–8 microns. The two layers of phosphor are seen in FIG. **5,** and each phosphor layer is from about 3 to 8 microns in thickness.

Microscopic examination of the individual phosphor layers **23** and **25** indicates good uniformity of thickness with the variation from the indicated average thickness being less than about plus or minus 0.5 microns. This means that the resultant screen has good color separation and purity.

The screened panel is then removed from the bath. In the application where brightness is not of concern, the conductive film **30,** may remain. However, for those applications where brightness is important the conductive substrate may be removed as more fully described in U.S. Pat. No. 3,525,679.

The faceplate **16** may then be assembled in the cathode ray tube seen in FIG. **1** and sealed by methods well known in the art. The bulb may also be provided with an aluminum coating **26** and may be applied in a well known manner by organic film technique. The organic film may be removed from beneath the aluminum during the normal bake-out tube which is about 10 minutes at 410°C.

It is found with the screen described herein that by an excitation energy of less than 6000 volts the second phosphor layer **25** will be excited so as to emit substantially red emissions. By increasing the voltage to a potential greater than 6000 volts, the emission will be from both layers and as a result of the mixture of red and green emissions the color to the viewer will be yellow. Increasing voltage will cause the color to shift more and more towards green, and at approximately 12–14 KV the emission color will be fully green.

It should be understood that a variety of cathodoluminescent phosphors can be used in practicing the present invention. It should also be understood that three or more thin phosphor layers of distinct materials can be so deposited to provide even a greater emission color variation dependent upon the excitation energy.

While the method of the present invention generally eliminates the necessity of providing a barrier layer between the phosphor layers, the electrophoretic deposition of the phosphor layer can be carried out with a barrier layer deposited between the phosphor layers if desired.

I claim:

1. A method of producing a multi-layer color cathodoluminescent display screen which produces light of varying color in response to electron excitation of varying energy, wherein individual distinct thin layers of finely divided cathodoluminescent phosphor materials of diverse color output are disposed upon an insulating light transmissive substrate with the individual layers being in intimate contact with the adjacent layer, which method comprises:

a. depositing a thin conductive film on the insulating light transmissive substrate;

b. electrophoretically depositing a front phosphor layer upon the thin conductive film which is maintained at a predetermined electrical potential, which front phosphor emits visible radiation of a predetermined color when electron excited, and which front phosphor layer substantially passes the emission from the other phosphor;

c. electrophoretically depositing at least one other phosphor layer directly upon the front phosphor layer, which other phosphor layer emits visible radiation of a distinct color diverse from the color emitted by the front phosphor, with the other phosphor layer thickness being determined to substantially completely absorb exciting electrons which have less than a predetermined energy level, while permitting passage of a portion of exciting electrons which have greater than a predetermined energy level to permit excitation of the front phosphor layer.

2. The method specified in claim **1,** wherein a thin protective conductive coating is deposited over the other phosphor layer.

3. The method specified in claim **1,** wherein the thin conductive film between the substrate and the front phosphor is removed after the plurality of phosphor layers are deposited on the substrate.

4. The method specified in claim **3**, wherein the thin conductive film comprises individual thin films, one atop the other, of aluminum over the substrate, gold over the aluminum, and indium over the gold.

5. The method specified in claim **1**, wherein the front phosphor layer and the other phosphor layer are each of uniform thickness of from about 3 to 8 microns, with the variation from the average thickness being less than about ± 0.5 microns.

6. A method of producing a multi-layer color cathodoluminescent display screen which produces light of varying color in response to electron excitation of varying energy, wherein individual distinct thin layers of finely divided cathodoluminescent phosphor materials of diverse color output are disposed upon an insulating light transmissive substrate with the individual layers being in intimate contact with the adjacent layer, which method comprises:

a. depositing a thin evaporable conductive metal film on the insulating light transmissive substrate;

b. electrophoretically depositing a front phosphor layer of uniform thickness of from about 3 to 8 microns upon the thin conductive metal film which is maintained at a predetermined electrical potential, which front phosphor emits visible radiation of a predetermined color when electron excited, and which front phosphor layer substantially passes the emission from the other phosphor;

c. electrophoretically depositing at least one other phosphor layer of uniform thickness of from about 3 to 8 microns directly upon the front phosphor layer with a smooth interface between the phosphor layers, which other phosphor layer emits visible radiation of a distinct color diverse from the color emitted by the front phosphor, with the other phosphor layer thickness being determined to substantially completely absorb exciting electrons which have less than a predetermined energy level, while permitting passage of a portion of exciting electrons which have greater than a predetermined energy level to permit excitation of the front phosphor layer.

7. The method specified in claim **6**, wherein the respective phosphor layers comprise finely divided phosphor materials having an average particle diameter of less than about 1.5 microns.

8. A cathode ray display device which produces light of varying color in response to electron excitation of varying energy and having a multi-phosphor layer display screen upon a light transmissive substrate prepared by the process of:

a. depositing a thin evaporable conductive metal film on an insulating light transmissive substrate;

b. electrophoretically depositing a finely divided front phosphor layer upon the thin conductive film which is maintained at a predetermined electrical potential, which front phosphor layer is deposited in a uniform thickness of from about 3 to 8 microns, which front phosphor layer emits visible radiation of a predetermined color when electron excited, and which front phosphor layer substantially passes the emission from the other phosphor;

c. electrophoretically depositing at least one other finely divided phosphor layer directly upon the front phosphor layer, which other phosphor layer emits visible radiation of a distinct color diverse from the color emitted by the front phosphor layer, with the other phosphor layer thickness being uniform to smoothly interface with the front phosphor layer, and which other phosphor layer thickness from about 3 to 8 microns thick to substantially completely absorb exciting electrons which have less than a predetermined energy level while permitting passage of a portion of exciting electrons which have greater than a predetermined energy level to permit excitation of the front phosphor layer.

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