Jan. 2, 1973 MASAHIRO NISHIZAWA ET AL 3,708,336
METHOD OF MAKING COLOR PHOSPHOR SCREEN
OF COLOR PICTURE TUBE
Filed Oct. 13, 1970 2 Sheets-Sheet 1

Fig. 1

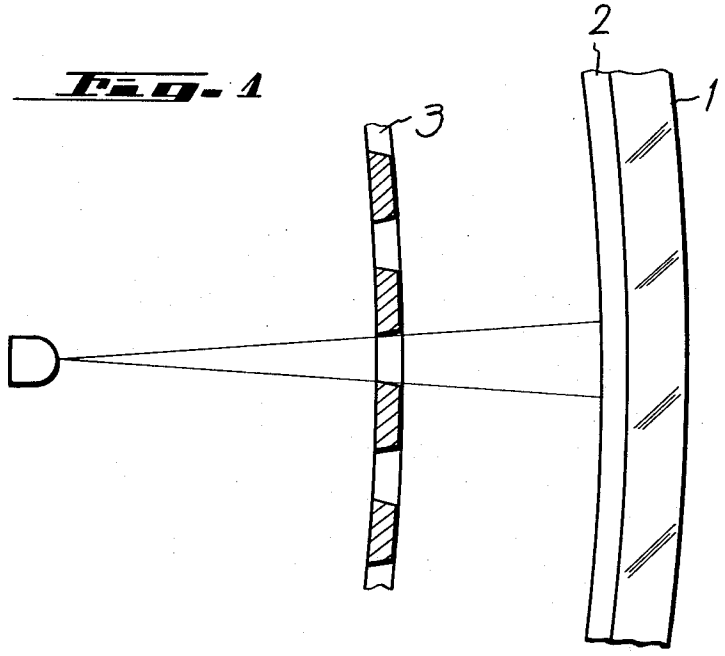
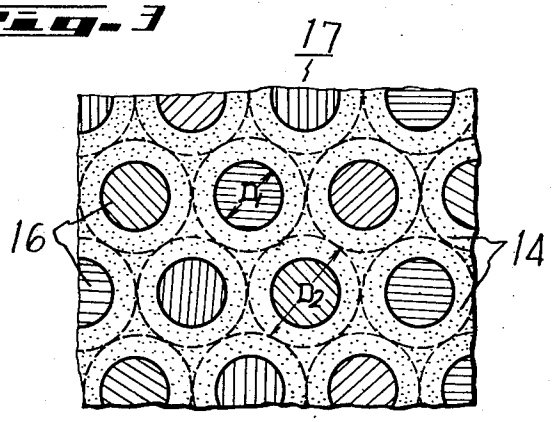


Fig. 3



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Fig. 2A

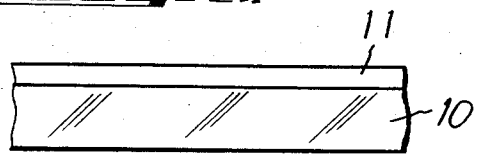


Fig. 2E

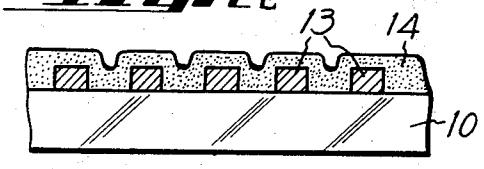


Fig. 2B

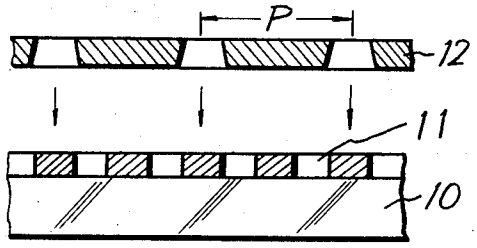


Fig. 2F

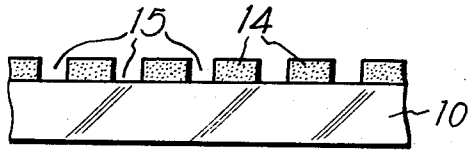


Fig. 2C

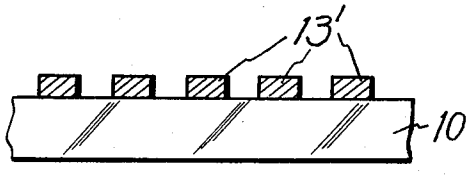


Fig. 2G

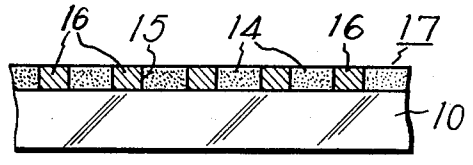
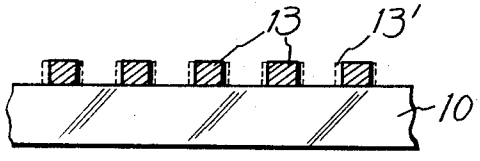


Fig. 2D



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3,708,336

METHOD OF MAKING COLOR PHOSPHOR SCREEN OF COLOR PICTURE TUBE

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Int. Cl. B44d 1/50
U.S. Cl. 117—33.5 CM 8 Claims

ABSTRACT OF THE DISCLOSURE

A method of making a color phosphor screen of a color picture tube in which a photosensitive material is coated on an inner surface of a faceplate of a color picture tube; the photosensitive material is exposed through a shadow mask; the exposed photosensitive material is developed to form temporary dots on the inner surface of the faceplate; the temporary dots are treated with a contracting agent in damped condition; the contracted dots are hardened; a block material is coated on the inner surface of the faceplate having formed thereon the hardened temporary dots; the temporary dots and the black material are removed to form void areas; and predetermined color phosphors are deposited on the void areas.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a method of making a phosphor screen of a color picture tube which is of particular utility when employed in the manufacture of three color phosphor dots of the phosphor screen.

Description of the prior art

There has heretofore been proposed a phosphor screen of a color picture tube affording improved brightness and contrast which is of the type that three color phosphor dots are deposited on the face of a front panel while each dot being spaced apart from adjacent ones at predetermined distance, a black material is deposited on the region between the three color phosphor dots to surround them and electron beams larger in diameter than those of the phosphor dots impinge upon the respectively corresponding three color phosphor dots.

The known color phosphor screen is made by the following method. Namely, temporary dots are formed on the faceplate at predetermined positions, that is, at those areas where the three color phosphor dots will be ultimately deposited, through the use of a shadow mask having apertures smaller in diameter than those of a shadow mask usually employed in the picture tube; a black material is coated all over the faceplate; the coated black material layer is treated with hydrogen peroxide (or the faceplate is treated with hydrogen peroxide after the formation of the temporary phosphor dots and then the black material is coated over the faceplate) to break the molecular chain of polyvinyl alcohol contained in the temporary dots; the temporary dots and the black material deposited thereon are removed to form void areas for the three color phosphor dots in the black material layer; the color phosphors are embedded in the void areas to form a phosphor screen; and the apertures of the shadow mask used in the making of the phosphor screen are enlarged in diameter by means of etching or the like, the shadow mask being assembled with the picture tube. Thus, the conventional method additionally involves the last-mentioned etching process.

Generally, in the making of the phosphor screen of the shadow mask color picture tube, when a photosensitive slurry coated on a faceplate are spaced apart from a shadow mask opposed thereto, a pattern projected onto the faceplate through the shadow mask is larger than that of the shadow mask. It is very difficult with the prior art to render the pattern of the shadow mask projected onto the faceplate equal to or smaller than that of the shadow mask.

SUMMARY OF THE INVENTION

Accordingly, the primary object of this invention is to provide a method of making a phosphor screen of color picture tubes which eliminates the aforementioned defects of the prior art.

Another object of this invention is to provide a method of making a phosphor screen of color picture tubes in which the borders lines of color phosphor dots and a black material are sharp.

Other objects, features and advantages of this invention will become apparent from the following description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing the manner in which a photosensitive slurry coated on the faceplate is exposed to light through a mask;

FIG. 2 is a sequence of steps involved in the manufacture of a color phosphor screen of a color picture tube in accordance with one example of this invention;

FIG. 3 is an enlarged fragmentary diagram of a phosphor screen of a color picture tube made according to this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

After a laborious study for rendering the pattern of a shadow mask 3 projected onto a photosensitive slurry 2 equal to or smaller than that of the shadow mask with the slurry 2 and the shadow mask 3 are spaced with each other as in the case of FIG. 1, the present inventors have found the following principle.

Namely, in the event that a photosensitive binder coated on the panel face which is composed of polyvinyl alcohol and ammonium dichromate is exposed to light, developed and is then, while in damped condition, treated with a solution of a sulfate such as ammonium sulfate, sodium sulfate, potassium sulfate, magnesium sulfate or the like, sodium hydrogen sulfate, potassium hydrogen sulfate, a nitrate such as potassium nitrate or the like, a nitrite such as sodium nitrite, a halide salt such as sodium chloride or the like, a phosphate such as potassium phosphate, di-sodium hydrogen phosphate, di-potassium hydrogen phosphate, di-lithium hydrogen phosphate or the like, sodium di-hydrogen phosphate, potassium di-hydrogen phosphate, lithium di-hydrogen phosphate, a carbonate such as sodium carbonate, a bicarbonate, or a solution of potassium acetate, organic sulfonic acid or like organic acid, the photosensitive binder contracts 25 to 30% at a maximum.

In accordance with the present invention three color phosphor dots are deposited on the phosphor screen at predetermined intervals and a black material is deposited between the three color phosphor dots to thereby provide for enhanced brightness and contrast of the phosphor screen of the color picture tube. The present invention resides in a method of making the phosphor screen of the color picture tube which comprises the steps of forming temporary dots on the faceplate at those areas to be ultimately occupied by phosphor dots of three colors,

coating a black material all over the faceplate, removing the temporary dots and the black material coated thereon to form void areas for the phosphor dots of the three colors and embedding predetermined phosphors in the void areas respectively, and in which a photosensitive agent composed of polyvinyl alcohol and ammonium dichromate is laid down on the faceplate of a cathode ray tube, exposed to light through a mask having a predetermined pattern and developed to obtain the temporary dots, the temporary dots are, while in damped condition, treated with a contracting agent to be contracted, hardened and rinsed, the temporary dots after rinsed being of the same size as that when contracted.

Turning now to FIG. 2, one embodiment of this invention will hereinbelow be described.

0.8 ml. of 10% ammonium dichromate solution is added to 50 ml. of 4% polyvinyl alcohol solution to obtain a photosensitive binder. The photosensitive binder is coated on a base plate **10** in the form of a layer **11** (FIG. 2A). Then, the photosensitive binder layer **11** is dried at a temperature of less than 40° C. and exposed through a shadow mask **12** to irradiation by light or electron beams emitted from light sources or electron guns placed at positions G (green), B (blue) and R (red), (FIG. 2B) the shadow mask **12** being such that the pitch P of apertures bored therein is 0.72 mm., the apertures at the central area of the mask are 0.37 mm. in diameter and those at the peripheral area are 0.32 mm. in diameter. Next, the exposed photosensitive binder layer **11** is developed and while in damped condition temporary dots **13'** of the photosensitive binder layer on the faceplate (depicted in FIG. 2C) are treated with a 3% ammonium sulfate solution and then dried, by which the temporary dots are contracted 25 to 30% to provide dots **13**. Namely, the diameters of the dots **13** are 0.26 mm. on the central area of the faceplate and 0.21 mm. on the peripheral area (FIG. 2D). The contracted temporary dots **13** have not completely hardened yet and include unreacted polyvinyl alcohol, and hence are required to be further hardened. (a) In the event that the temporary dots **13** are hardened by heating, the temperature is kept at higher than 100° C. for approximately 30 minutes and then the temporary dots **13** remain in the condition when contracted even after ammonium sulfate has been washed away with water. (b) In the case of achieving the hardening with light or electron beam, unreacted ammonium dichromate in the above development process flows out, so that the temporary dots **13** are treated with a solution of ammonium sulfate and ammonium dichromate added in an amount of 2% relative to the former and dried, thereafter being irradiated by light or electron beam. In such a case, the temporary dots **13** remain to be of the same size as that when contracted. The ammonium dichromate added is cross-linked with remaining polyvinyl alcohol. The concentration of ammonium dichromate, the intensity of light or electron beam, the irradiation time and so on can be changed at will.

The degree of contraction of the aforementioned temporary dots **13** increases with a decrease in the amount of hardening of the photosensitive binder layer composed of polyvinyl alcohol and ammonium dichromate. The same contraction results can be obtained even by coating on the base plate a photosensitive slurry which is produced by mixing a powdery material such as manganese oxalate into a polyvinyl alcohol solution. A black material **14** such as manganese dioxide is laid down by the aforementioned known method on the temporary dots **13** formed on the faceplate **10** (FIG. 2E). Next, the black material film **14** is treated with, for example, hydrogen peroxide or like material to remove the temporary dots **13** and the black material film coated thereon to leave void areas **15** for three color phosphors (FIG. 2F). Following this, phosphors **16** are embedded in the void areas **15** by slurry method or the like, thus providing a phosphor screen **17** of the color picture tube (FIG. 2G).

A description will be given in connection with the making of a phosphor screen of a 19-inch color picture tube using a photosensitive slurry produced by mixing manganese oxalate into a polyvinyl alcohol solution.

The first step is to coat uniformly all over the inner surface of a panel of the picture tube a photosensitive slurry composed of 20 grams of manganese oxalate ($M_nC_2O_4$), 50 ml. of 8% polyvinyl alcohol solution and 2.5 ml. of 10% ammonium dichromate ($(NH_4)_2Cr_2O_7$) solution. Then, the panel is assembled with a shadow mask and is exposed to irradiation by light emitted from light sources placed at those positions of three electron guns where they are actually located in picture tubes. This exposure is achieved three times each for each of the green, blue and red phosphors. After exposure, the shadow mask is disassembled from the panel and the panel is developed with water or hot water and dried, by which dots of manganese oxalate are formed at exactly the same positions, as those of the three color phosphor dots to be ultimately obtained. Thereafter, a suspension composed of 2 grams of graphite as a black material, 25 ml. of alcohol and 1 ml. of water glass (28%) is uniformly sprayed on the inner surface of the panel on which the dots of manganese oxalate have been formed, and is dried. After this, the inner surface of the panel is treated with a solution composed of hydrogen peroxide (H_2O_2 5% solution) and caustic soda (NaOH 10% solution), which results in the following chemical reaction.

$$M_nC_2O_4+2H_2O_2+2NaOH\rightarrow M_nO_2$$
$$+Na_2CO_3+CO_2+3H_2O$$

The dots of manganese oxalate are decomposed by the chemical reaction as above described and the dots of manganese oxalate and graphite attached thereto are completely removed by simple rinsing, thus leaving in the graphite layer void areas of the same diameter as that of the dots of manganese oxalate. The other remaining dots firmly adhere to the inner surface of the panel. Accordingly, manganese oxalate does not ever remain and has no influence upon brightness of the reproduced picture. Further, the border of the black material is sharp and brightness of the dots is not affected by the thickness of the coating, so that contrast and brightness of the picture can be well improved. It has been found that the same result can be obtained even in the case where the dots of manganese oxalate are treated with hydrogen peroxide prior to the coating of graphite and then treated with caustic soda or caustic potash.

With the method of this invention above described, the dots thus formed contract, and accordingly the reproduced picture becomes sharp and the dots can be reduced in size, as compared with the apertures of an optical mask.

FIG. 3 is an enlarged fragmentary plan view of the phosphor screen **17** produced by the present invention. As will be seen from the figure, the black material **14** is embedded between the phosphor dots **16** and the diameter D_1 of the phosphor dots **16** is made smaller than that D_2 of electron beams impinged thereon to thereby improve the brightness and contrast of the reproduced picture. Such a phosphor screen can be readily produced by this invention as has been described in the foregoing.

It will be apparent that many modifications and variations may be effected without departing from the scope of the novel concepts of this invention.

We claim as our invention:

1. A method of making a color phosphor screen of a color picture tube comprising the steps of coating a photosensitive material on an inner surface of a faceplate of a color picture tube, exposing the photosensitive material through a shadow mask, developing the exposed photosensitive material to form temporary dots on the inner surface of the faceplate, treating the temporary dots in

damped condition with a contracting agent selected from the group consisting of ammonium sulfate, sodium sulfate, potassium sulfate, magnesium sulfate, sodium hydrogen sulfate, potassium hydrogen sulfate, potassium nitrate, sodium nitrite, sodium chloride, potassium phosphate, disodium hydrogen phosphate, dipotassium hydrogen phosphate, dilithium hydrogen phosphate, sodium dihydrogen phosphate, potassium dihydrogen phosphate, lithium dihydrogen phosphate, sodium carbonate and potassium acetate, hardening the contracted temporary dots, coating a black material on the inner surface of the faceplate having formed thereon the hardened temporary dots, removing the temporary dots and the black material coated thereon to form void areas, and applying predetermined color phosphors to the void areas.

2. A method of making a color phosphor screen of a color picture tube as claimed in claim 1 wherein the photosensitive material is composed of polyvinyl alcohol and ammonium dichromate.

3. A method of making a color phosphor screen of a color picture tube as claimed in claim 1 wherein the hardening treatment takes place by heating.

4. A method of making a color phosphor screen of a color picture tube as claimed in claim 1 wherein the hardening treatment takes place by light.

5. A method of making a color phosphor screen of a color picture tube as claimed in claim 1 wherein the hardening treatment takes place by electron beams.

6. A method of making a color phosphor screen of a color picture tube comprising the steps of coating an inner surface of a faceplate of a color picture tube with a photosensitive material containing an oxalic acid salt difficult to dissolve in water, exposing the photosensitive material through a shadow mask, developing the exposed photosensitive material to form temporary dots on the inner surface of the faceplate, coating a black material on the inner surface of the faceplate having formed thereon the temporary dots, treating the temporary dots with one of sodium hydroxide, potassium hydroxide, mixture thereof and hydrogen peroxide to produce carbon dioxide, removing the temporary dots and the black material coated thereon by rinsing to form void areas, and applying predetermined color phosphors to the void areas.

7. A method of making a color phosphor screen of a color picture tube comprising the steps of coating an inner surface of a faceplate of a color picture tube with a photosensitive material containing an oxalic acid salt insoluble in water, exposing the photosensitive material through a shadow mask, developing the exposed photosensitive material to form temporary dots on the inner surface of the faceplate, treating the temporary dots with hydrogen peroxide, coating a black material on the inner surface of the faceplate having formed thereon the temporary dots, treating the temporary dots with one of sodium hydroxide, potassium hydroxide and mixture thereof to produce carbon dioxide, removing the temporary dots and the black material coated thereon by rinsing to form void areas, and applying predetermined color phosphors to the void areas.

8. A method of making a color phosphor screen of a color picture tube comprising the steps of coating an inner surface of a faceplate of a color picture tube with a photosensitive material containing an oxalic acid salt which is difficult to dissolve in water, exposing the photosensitive material through a shadow mask, developing the exposed photosensitive material to form temporary dots on the inner surface of the faceplate, treating the temporary dots with an agent selected from the group consisting of sodium hydroxide, potassium hydroxide, or mixtures thereof and hydrogen peroxide to produce carbon dioxide, coating a black material on the inner surface of the faceplate on which the temporary dots are formed, removing the temporary dots on the black material coated thereon by rinsing to form void areas, and applying predetermined color phosphors to the void areas.

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U.S. Cl. X.R.

96—36.1; 117—33.5 C