United States Patent

[11] 3,582,701

[72] Inventor **Nicholas Zeliotis**
Chicago, Ill.

[21] Appl. No. **811,060**
[22] Filed **Mar. 27, 1969**
[45] Patented **June 1, 1971**

[73] Assignee **Zenith Radio Corporation**
Chicago, Ill.

[54] **COLOR TUBE SCREEN WITH LIGHT-ABSORBING CERMET DEPOSITS**
5 Claims, 1 Drawing Fig.

[52] **U.S. Cl.** **313/92,** 29/25.17
[51] **Int. Cl.** **H01j 29/18,** H01j 9/22
[50] **Field of Search** ..... 313/92 B, 92; 29/25.17

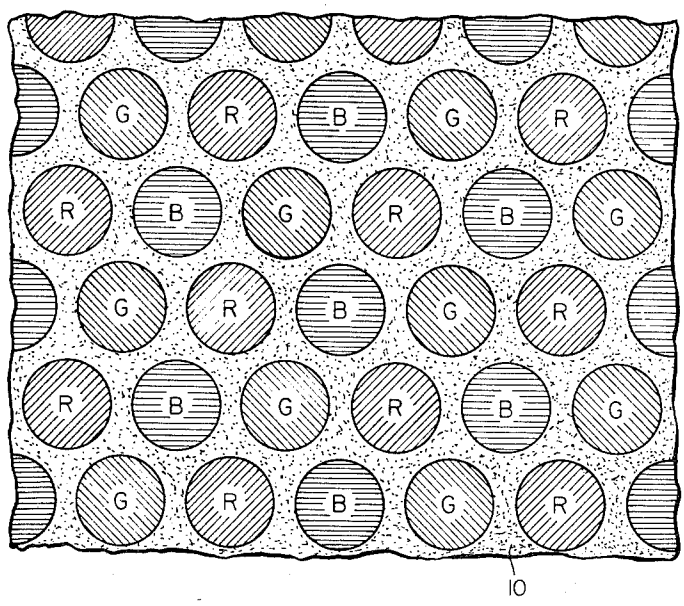
[56] **References Cited**

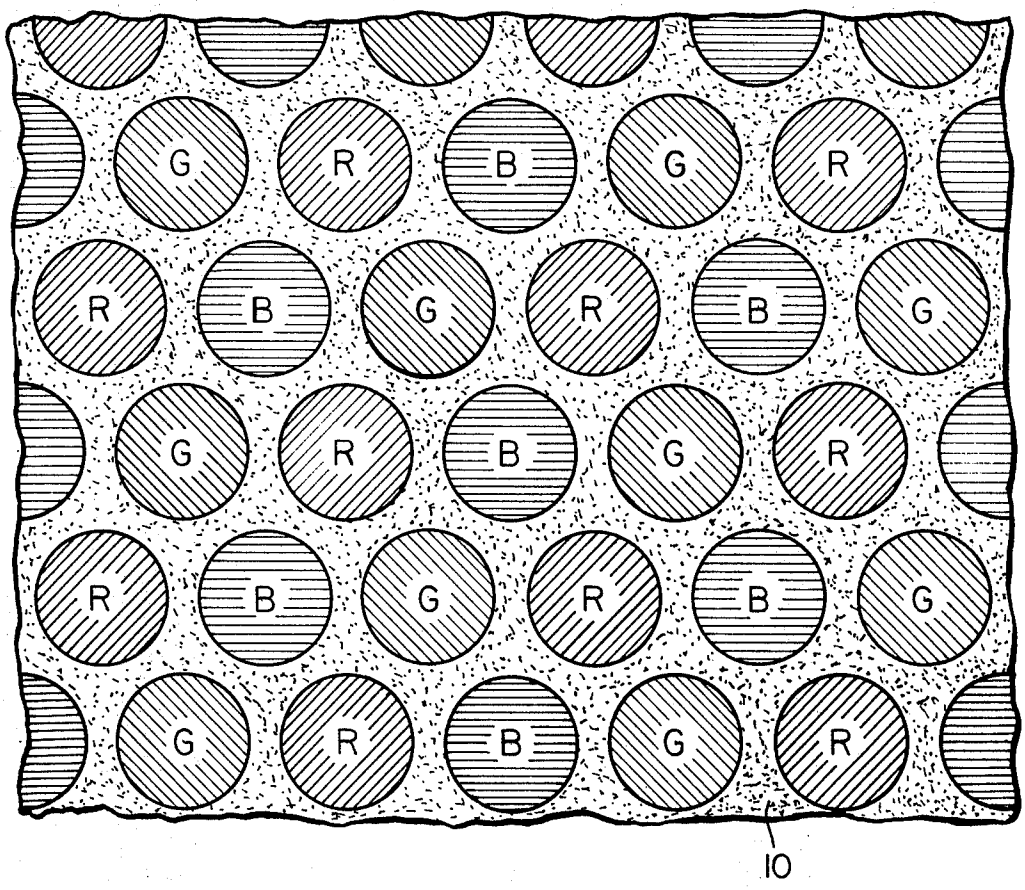
UNITED STATES PATENTS

2,675,740	4/1954	Barkley	351/165X
3,146,368	8/1964	Fiore et al.	313/92
3,365,292	1/1968	fiore et al.	313/92

Primary Examiner—Roy Lake
Assistant Examiner—V. Lafranchi
Attorney—Francis W. Crotty

ABSTRACT: A shadow mask type of color picture tube has a mosaic screen comprised of dots of green, blue and red phosphors which are individually smaller in size than the apertures of the mask. These dots are surrounded by a deposit of a light-absorbing cermet for absorbing visible ambient light incident on the face of the tube and comprising a mixture of nickel and nickel oxide or aluminum and aluminum oxide. In processing such a screen, the metal is vacuum deposited in an atmosphere of water vapor to cover the entire screen area with a cermet film and thereafter portions of the film overlying elemental areas of the screen intended to receive deposits of phosphor material are removed by etching.





Inventor
Nicholas Zeliotis

By Francis W. Crotty

Attorney

COLOR TUBE SCREEN WITH LIGHT-ABSORBING CERMET DEPOSITS

BACKGROUND OF THE INVENTION

A most striking advance in the development of color picture tubes, especially those of the parallax or shadow mask type, is described and claimed in U.S. Pat. No. 3,146,368, issued Aug. 25, 1964 and assigned to the assignee of the present invention. The specific disclosure of that patent concerns a color cathode-ray picture tube having a screen formed of dot triads each of which includes a dot of green, a dot of blue and a dot of red phosphor material. The phosphor dots are smaller in size than the apertures of the shadow mask, whereas in a conventional tube the phosphor dots and the apertures of the mask are essentially the same size. Having reduced the phosphor dots to a smaller diameter than the holes of the mask, there are significant areas of the screen which intervene or surround the phosphor dots and the reference patent teaches that a light-absorbing material or black pigment be placed in these areas and, accordingly, surround the phosphor deposits. Because of this physical arrangement, such a screen structure has become known as a "black surround" screen. As explained in the reference patent, it has greatly enhanced contrast and brightness properties.

In another U.S. Pat. No. 3,365,292, issued on Jan. 23, 1968, and also assigned to the assignee of the present invention, there is disclosed and claimed an attractive process for applying the black surround material. It features applying a material which normally exhibits low absorption of incident light but which decomposes to a black stable inorganic material, highly absorptive to light, when raised to a particular temperature such as that encountered in the normal bakeout step of color picture tube fabrication. Materials that are useful in this process are manganese carbonate and manganese oxalate each of which decomposes to black manganese dioxide when heated to the bakeout temperature.

The present invention concerns a color picture tube having a black surround screen and still another process for screening such a tube.

It is, accordingly, an object of the invention to provide a novel color picture tube having a black surround screen and a new process for screening such a tube.

It is another and particular object of the invention to provide an improved process for screening a black surround color picture tube.

SUMMARY OF THE INVENTION

A color picture tube embodying the present invention has a plurality of different phosphor materials deposited in respectively assigned ones of a multiplicity of elemental areas spaced from one another in a predetermined pattern over the screen portion of the tube. A black surround material in the form of a film of a cermet having light-absorbing properties surrounds such elemental areas of the screen.

The screening process comprises surrounding those elemental areas of the screen intended to receive a deposit of phosphor material with a film of a cermet having light-absorbing properties. The process further comprises depositing different phosphor materials in respectively assigned ones of those elemental areas. The order of these steps is not critical but there is a preference to applying the cermet film before depositing the phosphor materials.

BRIEF DESCRIPTION OF THE DRAWING

The features of the present invention which are believed to be novel are set forth with particularity in the appended claims. The invention, together with further objects and advantages thereof, may best be understood by reference to the single FIG. which is a fragmentary representation of the image screen of a color picture tube of the shadow mask type.

DESCRIPTION OF PREFERRED EMBODIMENT

Considering first the screen structure of a color picture tube, it is basically a panel of glass serving as a substrate to which the phosphor and light-absorbing materials are applied. It is of no particular consequence to the invention whether the screen be round, rectangular or any other configuration nor is it of any moment whether the phosphor deposits be arrayed in a repeating sequence of stripes, dots or other shape. But, for convenience, the invention will be described with particular reference to a screen of the dot triad type; a fragment of such a screen is represented in the drawing. Such a screen has a multiplicity of spatially separated deposits of phosphor representing an interleaving of three series of elemental picture areas spaced from one another in a predetermined pattern over the screen. For convenience, the legends G, B and R applied to the circles of the drawing designate deposits of green, blue, and red phosphors, respectively. The speckling 10 shown in the spaces which intervene or surround each of the multiplicity of phosphor dots denotes a film of a cermet having light-absorbing properties. While cermets, as such, are known in the art and are used, for example, in the fabrication of thin film resistors, their use as a light-absorbing pigment of a black surround screen of a color picture tube is believed to be unique and to have particular advantages.

Broadly speaking, cermets are mixtures of fine particles of metal and a dielectric and they are relatively easily prepared by cathodic sputtering or by vapor deposition, conducted in each case in a reactive gas such as air, oxygen or water vapor. It has been found that the oxidation process through which a cermet film or layer is prepared is more efficient and subject to better control when conducted with water or water vapor than with pure oxygen. If it be assumed that the particles of the metal employed in preparing a cermet film have sufficient energy to become oxidized if they collide with a water vapor molecule, the degree of oxidation is a matter of the probabilities of such collisions and the significant parameters determining this probability are the rate of evaporation of metal particles from a source, the number of molecules of water vapor in the atmosphere or constituting the reactive gas, the pressure of the gas and the distance from the metal charge to the substrate. If these parameters are related to the end that each metallic atom collides with a water vapor molecule the deposit will be pure metallic oxide but if the rate of evaporation of metal is increased beyond that point there will be an excess of metallic atoms and the deposition will be a mixture of very small metal particles dispersed in a dielectric since the metallic oxides generally have insulating properties. The rate of evaporation of the metal in relation to the concentration of water vapor molecules affects the color of the cermet film and using aluminum or nickel as the metal, for example, the color of the deposit will change from a light brown as the rate of evaporation increases to a dark color. Applicant has discovered that it is entirely feasible to have a black color or an efficient light-absorbing film with a cermet comprised of similar mixtures involving nickel, nickel alloy, aluminum and bismuth and their oxides. In particular, cermet film 10 for a color picture tube may be conveniently and efficiently formed as a mixture of nickel and nickel oxide or aluminum and aluminum oxide. As indicated in the literature, a number of metals are suitable in the preparation of cermet films and any may be employed as the screen component 10 of the tube under consideration so long as the cermet is compatible not only with the operation of the picture tube but also with its processing.

For convenience of reference, discussions of cermet films may be found in an article entitled, "Oxidized Aluminum for Passive Thin-Film Circuits" by Messrs. B. Pruniaux, G. Grunberg, I. Melnick and M. Cordelle, in the publication Thin Solid Films, 1 (1967/68), pages 417—427, Elsevier, Amsterdam Printed in the Netherlands, and in the article "Reactively Sputtered Cermet Resistors" by Clyde H. Lane, et al. Jan. 1967 document published by the U.S. Department of Com-

merce/ National Bureau of Standards/Institute for Applied Technology, Rome Air Development Center, Griffiss Air Force Base, N.Y., Processed for Defense Documentation Center, Defense Supply Agency.

In screening the structure represented in the drawing, there is a choice of applying the dots of different phosphor materials and then surrounding them with the light-absorbing cermet film or, alternatively, first preparing the cermet film and subsequently depositing the different phosphors. There is a preference to the latter because it relieves some of the screening tolerances that must otherwise be carefully observed where the phosphors are applied in advance of the black surround cermet. Accordingly, such a method will be described.

After the faceplate has been rendered chemically clean, it is placed in a vacuum deposition chamber which may be very similar to the aluminizing apparatus currently employed in the manufacture of color picture tubes for the purpose of vapor depositing a thin, electron permeable, conductive and light reflecting backing layer to the phosphor deposits. The chamber is charged with the metal that is to be evaporated and, for convenience, it will be assumed to be nickel which is readily evaporated by the use of a tungsten filament heater. With the vacuum chamber thus charged, it is pumped down or evacuated to a level of 10^{13} torr.

It is also necessary that the chamber be provided with a water vapor inlet and water vapor is then leaked in or admitted to establish a reacting or oxidizing atmosphere with a modified pressure, due to the presence of the vapor, of approximately 10^{11} torr. When these conditions have been established, the filament is flashed and the water vapor intake is turned off. As a consequence, the nickel is evaporated and a cermet film, in the form of a mixture of nickel and nickel oxide, is applied over the entire screen area by vapor deposition. This usually may be accomplished in a processing time of about 2 minutes, and if the deposition occurs under the stated conditions, e.g. in the presence of water vapor and at a pressure of about 10^{11} torr, the film will have excellent light-absorbing properties. If the vapor intake is continued for approximately the first 5 seconds of the film processing and is then interrupted, while the vacuum remains on continuously, the initial deposit will be a black, light-absorbing layer and the succeeding deposit will have a higher concentration of metal particles, will be less dark and will be more adhesive, serving to more firmly attach the film to the screen surface.

The screen, having thus been covered with a light-absorbing film, is removed from the vacuum deposition chamber for further processing to remove those portions of the light-absorbing film which overlie the multiplicity of elemental screen areas intended to receive deposits of phosphor materials. For that purpose a thin film of a photosensitive resist is applied to the coated screen. This resist has the property that it is normally insoluble in a particular solvent but is rendered soluble upon exposure to actinic energy such as ultraviolet light. After the photosensitive layer has been applied, the shadow mask is temporarily installed in its operative position relative to the screen and the screen is then exposed to ultraviolet light directed to the screen through the apertures of the shadow mask.

Since a three-color additive system is employed in commercial color television, it is necessary to have three exposures in each of which the light source is positioned to simulate the electron gun of the tube under process that is assigned to excite a particular color phosphor for which the exposure is being made. The three exposures may, of course, be made in a single exposure chamber having a light source that is selectively adjustable in position to represent each of three electron beams of the tube in sequence. Alternatively, three exposure chambers may be used which individually have a light source that is immovable in position but is located to simulate the electron beam of an assigned color. Whichever exposure method is elected and carried out, the photosensitive layer of the screen will have been exposed in a multiplicity of elemental areas representing the total number of elemental areas to receive a phosphor deposit. In short, the exposures establish latent images of the elemental areas which are developed by treating the photoresist layer with its solvent. Rinsing the layer with a solvent removes all of those portions that have been exposed to actinic energy and this, in turn, exposes the portions of the cermet film that overlie the elemental screen areas intended to receive deposits of phosphor material. Such portions of the cermet film must, likewise, be removed and for that purpose the film is subjected to an etchant. Where the cermet is formed of nickel and nickel oxide, an etchant such as a water solution of ferric chloride 136°—142° Baume will remove the portions of the cermet film that otherwise cover elemental picture areas of the screen that must receive deposits of phosphor material. The etchant is applied at room temperature by spraying or dipping for an interval of 5 to 10 seconds.

Having thus uncovered the portions of the screen that are to receive phosphor materials, such materials may be applied in conventional fashion. In the popular slurry-screening process, for example, this is accomplished by applying over the screen a second photosensitive layer of a material that includes a photosensitive resist having one of the phosphor materials in suspension. The resist ingredient in this case, however, has the property that it is rendered insoluble in a solvent in response to exposure to ultraviolet light. It is most convenient to use a water-soluble resist such as polyvinyl alcohol sensitized by ammonium dichromate. Such a resist carrying green phosphor and exposed to ultraviolet light from a source positioned to simulate the electron beam assigned to green for the tube under process, establishes images of the green phosphor dots. They may be developed by washing in water. Of course, the selective exposure will have taken place through the shadow mask of the tube and the phosphor dot images will be in proper registration with one set of holes that had previously been formed by removing portions of the cermet film. Accordingly, the green phosphor dots will now have been properly deposited. In similar fashion, deposits of blue and red phosphor are also made, completing the application of the black surround and the phosphor materials to the screen under process.

From this point forward, the customary filming and aluminizing steps take place and the screen structure is then baked to remove the resist ingredients by decomposition.

For a 25-inch rectangular tube a cermet film with good light-absorbing properties may be formed in the described process by charging the vacuum deposition chamber with approximately 700 mg. of nickel in pellet form. The spacing of the pellets from the substrate is approximately 5 inches. A suitable resist for use in removing selected elemental portions of the cermet film is Shipley AZ111 and the developer therefore is Shipley 303.

One advantage of the described order of applying the black surround and the phosphor materials is apparent from the fact that only so much of the phosphor deposit that fills the voids created in the cermet film is effective in image reproduction and, if in the screening process, the phosphor dots are in fact too large in size, the excess area merely overlaps the opaque cermet film and is of no particular consequence.

If desired, the cermet film may be covered with a metallic layer, either of the same metal from which the cermet has been formed or of a different metal. For example, where the cermet film is a mixture of nickel and nickel oxide, it is sometimes advantageous to apply a layer of aluminum over the cermet. This is a protective or barrier layer that prevents further oxidation of the metallic ingredients of the cermet film during the remaining process steps of the tube fabrication. To deposit an overlay of aluminum, it is only necessary to have an added tungsten filament heater in the vacuum chamber charged with an aluminum pellet and flashed after the cermet film has been deposited. The above-described process of forming voids in the cermet film through the use of an etchant is still valid and will remove the necessary parts of the overlay of aluminum in addition to the selected elemental areas of the cermet film. In-

stead of applying aluminum directly to the cermet film, there may be adequate protection afforded by the aluminum backing layer customarily applied to the screen.

Advantages realized with the described structure concern resolution and process time. The improvement in resolution results from the fact that the photosensitive resist applied over the cermet film as the first step of creating necessary voids in that film, is clear and has no particles in suspension as is the case where the black surround is applied in the form of a suspension in a photosensitive resist. The absence of particles in suspension avoids reflections of light within the photosensitive layer and improves resolution. Also, the photosensitive layer applied over the cermet may have a thickness of only 0.02 mg./cm.^{2} which is a thinner layer than used where the black pigment is carried by the resist in suspension. The thinner layer reduces the processing time by an approximate factor of 7.

Another advantage is that the light-absorbing property of the cermet layer has been measured to be about twice that of pigment layers applied with the slurry process. This in turn increases the tube contrast.

While particular embodiments of the invention have been shown and described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from the invention in its broader aspects, and, therefore, the aim in the appended claims is to cover all such changes and modifications as fall within the true spirit and scope of the invention.

I claim:

1. A color cathode-ray picture tube comprising:
a faceplate section having a screen portion;
a plurality of different phosphor materials deposited in respectively assigned ones of a multiplicity of elemental areas spaced from one another in a predetermined pattern over said screen portion of said tube;
and a film of a cermet having light-absorbing properties surrounding said elemental areas.

2. A color cathode-ray picture tube in accordance with claim 1 in which said cermet film is a mixture of nickel and nickel oxide.

3. A color cathode-ray picture tube in accordance with claim 2 in which said film is covered by a protective layer of aluminum.

4. A color cathode-ray picture tube in accordance with claim 1 in which said film is a mixture of aluminum and aluminum oxide.

5. A color cathode-ray picture tube in accordance with claim 1 in which said elemental areas are circular;
said phosphor deposits define dot triads on said screen individually including a dot of green, a dot of blue, and a dot of red phosphor; and
in which said cermet film surrounds each of said phosphor deposits.