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Baker

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[54] **PHOTOGRAPHIC METHOD FOR PRINTING VIEWING-SCREEN STRUCTURE INCLUDING TREATMENT OF EXPOSED COATING WITH AMMONIUM COMPOUND**

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[51] **Int. Cl.** **G03c 5/00**

[58] **Field of Search** ..... 96/36.1, 48 R, 49, 36; 117/33.5 CM, 33.5 C, 33.5 R

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[57] **ABSTRACT**

Method comprises (a) applying to a supporting surface for a viewing-screen structure of a cathode-ray tube a coating comprised of a dichromate-photosensitized organic binder, (b) exposing the coating of a pattern of actinic energy, including both heat energy and ultraviolet energy, (c) wetting the exposed coating with a dilute aqueous solution of an ammonium compound, such as ammonium oxalate, (d) and flushing the coating with an aqueous solvent to remove those portions of the coating that have been hardened solely by heat energy, while retaining portions of the coating that have been hardened by ultraviolet energy.

10 Claims, No Drawings

PHOTOGRAPHIC METHOD FOR PRINTING VIEWING-SCREEN STRUCTURE INCLUDING TREATMENT OF EXPOSED COATING WITH AMMONIUM COMPOUND

BACKGROUND OF THE INVENTION

This invention relates to a novel photographic method for printing a viewing-screen structure, particularly for an apertured-mask-type color-television picture tube.

A commercial color-television picture tube of the apertured-mask type is a cathode-ray tube which includes a screen structure comprised of a multiplicity of red-emitting, green-emitting and blue-emitting phosphor elements on the inner surface of the viewing window of a faceplate panel of the tube. An apertured mask (also called shadow mask), positioned in the panel in closely spaced relation with the phosphor elements, aids in selectively exciting the phosphor elements.

In order to make a television picture with suitable resolution and color purity, the process of forming the phosphor elements must be capable of producing a very large number of phosphor elements of relatively small and uniform size which are accurately positioned with respect to one another. In one process for printing the phosphor elements, the inner surface of the viewing window is coated with a mixture comprised of phosphor particles, polyvinyl alcohol, and a dichromate sensitizer such as ammonium dichromate for the polyvinyl alcohol. Actinic energy is projected from a small area source through the apertured mask incident upon the coating. The mask functions as a photographic negative (or positive) to transmit a pattern of energy, which produces in the coating regions with greater solubility and regions with lesser solubility. The exposed coating is developed by flushing with an aqueous solvent, until the more soluble regions of the coating are removed by solvent action, leaving the less soluble (hardened) regions adhered to the supporting surface.

It is known that the size and thickness of the phosphor elements are determined in part by various parameters including the geometry of the parts of the system, the constitution of the coating, the amount of heat and light to which the coating is exposed, and the development of the exposed coating. Generally, the greater the total amount of heat and ultraviolet energies employed to expose the coating, the larger will be the phosphor elements formed. Since the phosphor elements are closely spaced, variations in the size of the phosphor elements may lead to problems in the operation of the tube. Overexposed portions of the coating may produce oversized elements which may overlap adjacent elements, producing color impurity in the video picture. Underexposed portions may produce elements which do not adhere to the supporting surface or may produce undersized elements which may result in poor color purity and/or reduced brightness in the video picture. The "exposure" or "total energy" per unit area is the summation of the incremental actinic energies including heat energy and ultraviolet energy, applied to the coating.

There is considerable variation in the exposure across the field of a single viewing screen. Some regions are affected by heat energy alone, and some regions are affected by a combination of heat energy and ultraviolet energy. This difference may occur in several ways;

for example, over the entire image by a flood exposure of either heat or ultraviolet; at the image edges by a penumbra produced by light from a finite light source projected through a mask or stencil, or by distortions or aberations in the optical system, or by light scattering (diffusion) in the coating. In any of these instances, it may be desirable during development to distinguish between those regions which have been affected by ultraviolet energy or a combination of ultraviolet energy and heat energy and those regions that have been affected by heat energy alone or have not been affected at all.

SUMMARY OF THE INVENTION

The novel method for printing a viewing-screen structure comprises (a) applying to a supporting surface a coating comprised of a dichromatizable organic binder such as polyvinyl alcohol, a dichromate photosensitizer therefor and, optionally, particles of screen-structure material; (b) exposing the coating to a pattern of actinic energy including both heat energy and ultraviolet energy; (c) wetting the exposed coating with a dilute aqueous solution of an ammonium compound, such as ammonium oxalate; and (d) developing said coating by flusing the coating with an aqueous solvent to remove the more soluble portions and those less soluble portions of said coating that have been hardened (rendered less soluble) by heat energy alone, while retaining those less soluble portions that have been hardened (rendered less soluble) by ultraviolet energy.

By wetting the exposed coating with a dilute aqueous solution of an ammonium compound prior to or during development of the coating, undesired portions of the coating that have been hardened by heat energy alone are removed during the development step. The novel method may be used for removing the undesired portions of the coating which were previously retained during development. Or, the exposure of the entire field may be lengthened so that the entire coating is more fully exposed by ultraviolet energy, and yet, after development, the undesired portions are removed. The novel method may thereby be used to improve the adherence of the desired exposed portions of the screen structure.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENT

Example

Prepare a coating composition of the following formulation:

125 grams blue-emitting, silver-activated zinc sulfide phosphor,

138 grams **10** weight percent aqueous solution of polyvinyl alcohol having an average molecular weight of about **170,000** to **220,000,**

11 grams **10** weight percent aqueous solution ammonium dichromate, and

268 grams deionized water.

The coating composition is carefully mixed and the viscosity adjusted to be in the range of about **10** to **80** centipoises. The formulation is then flow coated upon the inner surface of the faceplate of a **23**-inch rectangular color-television picture tube and dried. The apertured mask for the faceplate is then inserted in the mounts provided therefor and the faceplate assembly positioned upon a lighthouse platform. Ultraviolet light from the small-area light source in the light house is

projected through the mask which permits a pattern of light to fall incident upon and to expose the coating for about **11** minutes. The faceplate panel is then removed from the lighthouse and the mask removed from the faceplate panel. The exposed coating is then wetted with a **0.5** weight percent aqueous solution of ammonium oxalate applied by spraying or fogging the solution onto the coating. With the coating still wet and preferably within about **10** seconds of the completion of applying the ammonium oxalate solution, the coating is developed by flushing with water to remove the still soluble portions of the coating together with those portions of the coating that have been insolubilized solely by heat. Those portions of the coating that have been insolubilized by ultraviolet light or a combination of heat and ultraviolet light are retained in place. By applying an aqueous ammonium oxalate solution to the coating, normal-sized phosphor dots are deposited with about **150** percent of the light exposure normally employed. However, the adherence of the dots is markedly improved with substantially no change in dot size.

GENERAL CONSIDERATIONS

The novel method may be used to print various viewing-screen structures by a photographic process. Dot screens and line screens are examples. By "viewing-screen structure" is meant any component part of a viewing screen for a display device; for example, a luminescent layer, or a light-absorbing layer for a cathode-ray-tube target. The novel method may be used to expose a layer comprised of a mixture of photobinder and particles, or to expose a layer of a clear photobinder, and then phosphor particles or light-absorbing particles may be deposited on the exposed areas. In the example, a phosphor-screen structure is deposited directly by exposing a layer comprised of phosphor particles mixed with a photobinder. An alternative method is to expose a layer of clear photobinder, then deposit phosphor particles thereon and then remove the more soluble portions of the photobinder and the overlying and/or embedded phosphor particles. Another method for preparing a phosphor-screen structure is to expose a layer of clear photobinder, remove the more soluble portions thereof, then deposit phosphor particles thereover and finally remove the less soluble portions of the photobinder layer with the phosphor particles thereon and/or therein, leaving phosphor particles in the portions previously occupied by the more soluble portions of the photobinder layer. The novel process may also be used to produce nonluminescent screen structures, such as a light-absorbing matrix for example, as described in U.S. Pat. No. **3,558,310** to E. E. Mayaud. An example of this method is to expose a clear photobinder layer to a light image, to remove the more soluble portions thereof, then to deposit light-absorbing particles such as fine-particle graphite thereover, then to remove the less soluble portions of the photobinder layer with the light-absorbing particles thereon, leaving the light-absorbing particles in the portions previously occupied by the more soluble portions of the photobinder layer. Thus, the novel method may be used to photodeposit either luminescent or nonluminescent screen structures.

The example illustrates the use of the novel method to prepare a screen for a color-television picture tube by the slurry process. Many suitable coating formulations for the novel method applied to the slurry process are described in U.S. Pat. No. **3,269,838** to T. A. Saulnier, Jr. Generally, the coating formulation is comprised of a dichromatizable organic binder, a dichromate photosensitizer for the binder, and particles of screen-structure material. The organic binder may be an organic colloid, such as gelatin or glue, but is preferably polyvinyl alcohol having a molecular weight greater than about **120,000.** The binder must be "dichromatizable"; that is, capable of being rendered photosensitive with dichromate ions. The photosensitizer may be any soluble dichromate such as sodium dichromate, potassium dichromate, or ammonium dichromate. The photosensitizer may be present in amounts of **2** to **20** weight percent of the weight of water-soluble polymer present. The screen-structure material may be, for example, luminescent material, inert material, or light-absorbing material, which is to be photodeposited as a screen structure. The coating may, if desired, include a resin, such as an acrylate copolymer, which is not rendered photosensitive by dichromate ions.

The coating is exposed to any actinic radiation such as infrared rays, visible light rays, or ultraviolet light rays. Suitable exposure equipment is described in the art, such as the lighthouse described in U.S. Pat. No. **3,592,112** to Harry R. Frey, which employs a collimator. A similar lighthouse which does not employ a collimator may be used, and such a lighthouse produces similar effects with shorter exposures. Significant qualities of the exposure are that it includes both heat energy and ultraviolet energy, and that the coating regions that are insolubilized by these energies are not identical. The normal necessary exposure is determined empirically to provide developed exposed areas of a prescribed size with adequate adherence to the supporting surface. With significantly longer exposures; that is, with about **125** to **200** percent of the normal necessary exposure, the exposed areas after development are oversized and frequently overlap on one another.

After exposure, the coating is wetted with a dilute aqueous solution of an ammonium compound; such as ammonium hydroxide; a salt of an organic acid, such as ammonium oxalate, ammonium formate, ammonium citrate, ammonium acetate; or a salt of an inorganic acid, such as ammonium chloride, ammonium nitrate; and ammonium carbonate. By "dilute" is meant concentrations of about **0.01** to **2.0** weight percent and preferably about **0.5** to **1.0** weight percent of the aqueous solution. The solvent in the dilute aqueous solution of ammonium compound may consist only of water or may include a portion of alcohol or other nonaqueous liquid that is miscible in water.

The effect of the ammonium compound solution is to act on the chromium ions in the reverse manner of a short flood actinic infrared exposure of the coating. This is believed to cause some trivalent chromium ions in the coating to be converted back to hexavalant ions. The ammonium compound solution dissolves only the heat-hardened coating and, unlike dilute solutions of oxidizing agents, does not attack the ultraviolet-hardened coating. Thus the novel method is self-limiting in its action on the coating. By using a dilute solution of an ammonium compound, the effect may be adjusted to be just sufficient after development to bring the exposed areas down to size and/or to improve the adherence of the exposed areas to the supporting surface, depending upon the trade-offs made with other

parameters in the method. This may require longer exposures to be used.

Exposure techniques that use shadowing (as in the example) or projection usually have a penumbra along the margins of the lighted areas of the pattern of actinic radiation. Usually, this marginal region in the coating is principally heat hardened and may be advantageously acted on by the novel method without adversely affecting the ultraviolet-exposed or unexposed regions. The size of the penumbra may be enlarged by employing larger diameter collimators (e.g., **150** to **200** mils) in the lighthouse, and may be reduced by employing smaller diameter collimators (e.g., **80** to **140** mils). Where a short flood exposure is employed to improve adherence, the novel method may be used to remove any underexposed coating material in the regions intended to be unexposed.

The solution may be applied to the coating by fogging, spraying, dipping, soaking, flushing, pouring, or other application techniques. The action of the ammonium compound solution may be almost self-limiting in another respect. Where the solution is applied to a dry coating, the coating takes up a limited amount of solution up to saturation. Any excess solution beyond this has essentially no effect on the exposed coating. The solution may be applied as a separate step or as the initial portion of the development step.

The time that the ammonium solution is permitted to act on the exposed coating is not critical. Time variations may, however, cause minor variations in the effectiveness of the treatment. It is preferred that the development step start about **10** seconds or less after the completion of the wetting step. This permits suitable process control on automatically operating production equipment.

The development of the wet coating is conducted in the usual way by flushing the coating with an aqueous solvent, which may be deionized water with or without additives present. The flushing may be by dipping or spraying or other method of application which will carry away the unexposed areas of the coating and leave the exposed areas in place.

The following are some solutions, in addition to the ammonium oxalate solution disclosed in the example, of nonoxidizing, nonreducing ammonium compounds which may be used in the novel method.

Ammonium Formate Solution - Dissolve at room temperature **3.0** grams of chemically pure ammonium formate in **997** grams of demineralized water. The pH of the solution should be about **5.0** to **6.0.**

Ammonium Citrate Solution - Dissolve at room temperature **4.0** grams of chemically-pure grade ammonium citrate in **996** grams of demineralized water. The pH of the solution should be about **5.0** to **6.0.**

Ammonium Nitrate Solution - Dissolve at room temperature **6.0** grams of reagent-grade ammonium nitrate in **994** grams of demineralized water. The pH of the solution should be about **4.0** to **5.0.**

Ammonium Hydroxide Solution - Mix at room temperature **200** grams of reagent-grade **10%** ammonium hydroxide with **800** grams of demineralized water. The pH of the solution should be about **10.0** to **11.0.**

Ammonium Chloride Solution - Dissolve at room temperature **8.0** grams of reagent-grade ammonium chloride in **992** grams of demineralized water. The pH of the solution should be about **4.5** to **5.5.**

There are patents in the photographic art which disclose processes which bear a resemblance to the novel method, but which are distinguishable. For example, U.S. Pat. No. **3,706,558** to H. R. Frey discloses a process comprising applying a dilute solution containing a mild reducing agent, such as hydroquinone, to an exposed coating comprised of a dichromated colloid, such as dichromated polyvinyl alcohol; and then developing the coating. In the Frey process, the reducing agent acts on the partially hardened regions of the coating to insolubilize them so that they are retained during development. In the novel method, the ammonium compound solution is not reducing and does not insolubilize partially hardened regions of the coating, but acts to solubilize coating portions that have been hardened solely by heat. U.S. Pat. No. **3,558,310** to E. E. Mayaud discloses a process comprising developing an exposed coating comprised of dichromated polyvinyl alcohol; and then treating the developed image with a dilute aqueous solution of a chemically digestive agent, such as hydrogen peroxide, to erode the edges of the retained coating regions. In the Mayaud process, all of the disclosed chemically digestive agents are oxidizing to the coating and erode the fully hardened portions of the coating, albeit at a slower rate. The ammonium compound solutions of the novel method are not oxidizing and do not erode the fully hardened portions of the coating, but act only on those coating portions that have been hardened solely by heat.

I claim:

1. A photographic method for printing a viewing-screen structure upon a supporting surface comprising:

a. applying to said supporting surface a coating comprised of a dichromatizable organic binder and a dichromate photosensitizer for said binder,

b. exposing said coating to a pattern of actinic energy, said exposure including both heat energy and ultraviolet energy,

c. wetting said exposed coating with a dilute aqueous solution of an ammonium compound,

d. and then flushing said exposed coating with an aqueous solvent to remove the more-soluble portions of the coating and those less-soluble portions of said coating that have been exposed solely to heat energy, while retaining in place the less-soluble portions of said coating that have been exposed to ultraviolet energy.

2. The method defined in claim **1** wherein said solution is a **0.01** to **2.0** weight-percent solution of an ammonium compound selected from the group consisting of ammonium hydroxide, ammonium oxalate, ammonium formate, ammonium citrate, ammonium acetate, ammonium chloride, ammonium nitrate and ammonium carbonate.

3. The method defined in claim **1** wherein said dichromatizable organic binder is a polyvinyl alcohol.

4. The method defined in claim **3** wherein said ammonium compound is a salt of an organic acid.

5. The method defined in claim **3** wherein said ammonium compound is a salt of an inorganic acid.

6. A method for printing a phosphor-viewing-screen structure for a cathode-ray tube upon a supporting surface comprising:

a. applying to said supporting surface a coating comprised of polyvinyl alcohol, a dichromate photosensitizer for said alcohol, and particles of phosphor for said screen structure,

b. projecting a pattern of actinic energy upon said coating, said exposure including both heat energy and ultraviolet energy, thereby reducing the solubility of the exposed portions of said coating,

c. wetting said exposed coating with a dilute aqueous solution of an ammonium compound,

d. and then flushing said wet coating with an aqueous solvent to remove the unexposed more-soluble portions of said coating and the less-soluble portions of said coating that have been exposed solely to heat energy while retaining in place the less-soluble portions of said coating that have been exposed to ultraviolet energy.

7. The method defined in claim **6** wherein said ammonium compound is the salt of an inorganic acid and is present in concentrations of **0.01** to **2.0** weight percent of said aqueous solution.

8. The method defined in claim **6** wherein said ammonium compound is the salt of an organic acid and is present in concentrations of **0.01** to **2.0** weight percent of said aqueous solution.

9. The method defined in claim **6** wherein said ammonium compound is present in said solution in concentrations of about **0.1** to **0.5** weight percent.

10. The method defined in claim **6** wherein step (d) is carried out within **10** seconds after the completion of step (c).

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