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PROCESS FOR FABRICATING MULTICOLOR IMAGE SCREENS

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ABSTRACT OF THE DISCLOSURE

In a process for fabricating color television picture tube screens which includes the steps of forming a layer of a photosensitive composition on the faceplate on which the colored-light-emissive phosphors are to be deposited, selectively exposing those regions of the photosensitive layer, with actinic radiation, and selectively removing the unexposed regions of the layer, the improvement of having uniformly distributed through the photosensitive layer numerous minute particles (preferably including calcium phosphate dibasic) each of which has an equivalent spherical diameter of less than about five microns and is adapted to scatter actinic radiation incident thereon. Because the numerous minute particles scatter the incident actinic radiation numerous times through very small distances within each region undergoing exposure, uniform hardening of the photosensitive composition takes place throughout each exposed region and close control of the shape, size, hardness and tackiness of each exposed region is thereby afforded. Hence deposition of a uniform density of phosphor throughout each exposed region is facilitated.

INTRODUCTION

The shadowmask type of color television picture tube typically comprises a light-emissive screen including a transparent glass faceplate to which are affixed phosphor dots respectively emissive of red, green and blue light when impinged by an electron beam. The phosphor dots emissive of light of each color are arranged to form a repetitive pattern on the faceplate. The shadowmask tube also comprises three electron guns directed toward the screen, and a perforated plate (the shadowmask) positioned between the three electron guns and the screen. For faithful color reproduction, the arrangement and size of the phosphor dots, the arrangement of the holes in the shadowmask, the diameter of these holes, the positioning of the shadowmask between the screen and the three electron guns, and the positioning and respective orientations of the three guns with respect to shadowmask and screen must be such that, when the three electron beams respectively emitted by the three guns are scanned across the shadowmask, the portion of any one beam passing through holes in the shadowmask impinges only on phosphor dots emissive of light of a given color. To obtain this result in a picture tube providing high-resolution color reproduction, each phosphor dot must be correctly positioned on the faceplate of the tube, and the shape and size of each dot, e.g., its circularity and diameter, must conform closely to the shape and size called for by the design of the tube. To obtain from the picture tube the brightest image obtainable with the specific phosphors employed, each phosphor dot must have a high phosphor density and contain a sufficient quantity of phosphor, and substantially all of the phosphor contained in each dot must be impinged by electrons of the beam scanning that dot. In addition, the phosphor must be distributed substantially uniformly throughout each dot.

To obtain the required placement and configuration of the phosphor dots on the screen, it has been found desirable to deposit the dots photographically, using the shadowmask as a photographic mask to control the exposure of a light-sensitive layer on the screen.

Heretofore, it has been difficult to deposit, on the faceplate of a shadowmask tube, phosphor dots which have a high density of phosphor distributed uniformly throughout each dot and at the same time are positioned accurately and have the required shape and size. To obtain dense dots, many manufacturers have employed the so-called slurry method of photodeposition. In this method, the phosphor to be deposited is mixed with a solution of photosensitive material to form a slurry. The faceplate is coated with this slurry. Then those regions of the photosensitive coating overlying areas on the faceplate on which dots of the phosphor are to be deposited are exposed to actinic radiation through the shadowmask. Thereafter solely the unexposed regions of the coating are removed from the faceplate by dissolving them selectively with an appropriate solvent. Phosphor dots composed of a phosphor emissive of a different color are deposited by repeating the foregoing steps with a slurry including particles of the latter phosphor.

The slurry process has several limitations. Because the photosensitive coating contains many phosphor particles and because the phosphor absorbs a considerable amount of the actinic radiation used to expose the coating, a relatively long exposure of the coating is required to expose the portion of the coating adjacent the faceplate sufficiently to prevent this portion from being undermined by the solvent employed to remove unexposed portions of the coating. For example, an exposure of 8 to 12 minutes may be required when the coating contains a phosphor having a white body color, and as much as 25 minutes may be required when the coating contains a phosphor having a body color other than white, e.g. orange. However such long exposures are undesirable because they slow the mass-production of tubes.

The phosphor present in the photosensitive coating also makes it difficult to control accurately the shape and size of dots made by the slurry process. Typically, the phosphor particles present in the slurry are irregularly shaped. In addition many of these particles are relatively large, e.g. 10 to 20 microns, and are spaced relatively far from each other to permit sufficient penetration of the exposing radiation to the substrate. Under these conditions the actinic radiation incident on the photosensitive coating frequently is scattered by the phosphor particles to regions of the photosensitive coating well beyond the perimeters of those areas thereof on which the exposing radiation impinges after passing through the holes in the shadowmask. Since a relatively long exposure is needed to expose the portion of the photosensitive coating adjacent the faceplate sufficiently to obtain satisfactory adhesion of the dots to the faceplate, this outward "growth" of the exposed region often is considerable. Furthermore, since relatively large gaps exist between some of the phosphor particles, the pattern of exposure produced by the scattered radiation cannot be predicted accurately. As a result, the configuration of the dots produced by the slurry method cannot be controlled precisely.

Moreover, if (in an attempt to improve the size and shape of the exposed regions by reducing exposure time) only a thin layer of slurry is used, the resultant phosphor dots still are frequently unsatisfactory because voids (absences of phosphor particles) occur in the dots. Such voids reduce the total light output of the dots and produce non-uniform light emission across the areas of those dots in which such voids occur. Furthermore, because the thickness of the slurry is reduced, the quantity of phosphor deposited also is reduced, often to levels which give unsatisfactorily low light output.

To allow for the fact that the "growth" of the exposed regions of the photosensitive layer often cannot be controlled accurately in the slurry process, it is necessary when using this process to make the holes in the shadowmask through which the photosensitive coating is exposed sufficiently small to constrain the exposing radiation passing therethrough to areas of the photosensitive coating substantially smaller than the areas which the completed phosphor dots are to have. However any reduction in the diameter of the holes of the shadowmask below the diameter required by the electron optics of the tube is undesirable because it reduces the light output of the screen and increases the heat generated in the shadowmask by the impingement thereon of the electron beams of the completed tube.

To provide more accurate control over the shape and size of the phosphor dots, other phosphor deposition processes have been suggested in which a translucent photosensitive film free of phosphor is used in place of the phosphor-containing photosensitive coating used in the slurry process, and the phosphor is applied to this film only after exposure thereof. In one such process, the phosphor is applied, immediately after exposure of the film, to a surface of the film (e.g., by dusting, settling, low-pressure spraying or in a slurry). Then the unexposed portions of the film and the phosphor adherent thereto are removed selectively (see e.g., U.S. Pat. No. 2,950,193 of P. D. Payne, Jr.).

In another such process, unexposed portions of the film are removed selectively immediately after exposure of the film and before the phosphor is applied thereto. Then the phosphor is embedded throughout each of the exposed portions of the film by projecting dry phosphor particles thereagainst with velocities sufficient to cause penetration of the phosphor particles throughout the exposed portions. This process is described and claimed in my copending U.S. patent application Ser. No. 452,747, filed May 3, 1965, entitled "Process for Depositing Particulate Solid Material on Selected Portions of a Substrate," assigned to the assignee of the present application, now Pat. No. 3,428,454, granted Feb. 18, 1969.

Because the photosensitive film used in the foregoing processes contains no phosphor, much less light is absorbed and scattered within the film than in the slurry process. As a result, the time required to expose the photosensitive film is substantially shorter, and the configuration of the deposited phosphor dots is more closely controllable, than in the slurry process. Moreover, when the process described and claimed in my above-identified patent application is employed, satisfactorily high phosphor densities are readily obtained.

However, processes employing translucent phosphor-free photosensitive films sometimes undesirably produce phosphor dots in which the phosphor density and quantity varies considerably through the dot in directions parallel to the faceplate. For example, some phosphor dots made by these processes are "doughnut"-shaped. These variations in phosphor density and quantity are undesirable because different regions of such dots emit different amounts of light and because a smaller total amount of light is obtained from such dots then from dots which contain the same optimum density and amount of phosphor particles at all regions thereof.

"Doughnutting" and other undesirable spatial variations in the phosphor density of the dot are brought about by uneven illumination by the exposing radiation of the region of the photosensitive film employed in fabricating the dot. Such uneven illumination tans unevenly the region undergoing exposure. Consequently, when, after exposure, the phosphor particles are dusted onto the exposed region, more cling to the less thoroughly exposed (and therefore tackier) surface portions of the exposed region than to the more thoroughly exposed (and less tacky) surface portions thereof. Moreover when in accordance with the process described and claimed in my application Ser. No. 452,747, now Pat. No. 3,428,454, the exposed regions are soaked and then particles of dry phosphor are projected thereagainst, more phosphor particles are able to embed themselves in the softer, less thoroughly exposed portions of the exposed regions than in the harder, more thoroughly exposed portions of the exposed regions.

"Doughnutting" generally is caused by one or both of the following:

(1) The beam of actinic radiation (e.g., ultraviolet light) passing through a hole in the shadowmask may have a nonuniform intensity over its cross-section, characteristically being less intense near the edge of this cross-section than near the center thereof. This variation in intensity occurs because the source of actinic radiation (e.g., an ultra-violet-emissive arc lamp and quartz collimator in a typical "lighthouse") has an emissive area substantially larger than a point. By reason of this intensity variation across the beam, the exposure of the periphery of the region on which such a beam is incident is less complete than the exposure of the central portion of such region.

(2) Light is reflected from the interface between the faceplate and the film into regions of the photosensitive layer outside the regions on which the beams of exposing radiation are directly incident. This reflected light exposes the portions of the film on which it is incident. Since the amount of this reflected light is substantially smaller than the amount of light directly incident on the film, the exposure produced thereby is less complete than the exposure produced by the directly-incident light.

As a result of the foregoing, the peripheries of the exposed regions are softer and tackier than the central portions thereof. Hence these peripheries are able to be penetrated by more phosphor particles than can penetrate the central portions, and more phosphor particles adhere to the peripheral surface portions than to the central surface portions. As a result "doughnutted" dots are obtained.

The objects of my invention are as follows:

To provide an improved process for depositing particulate solid material on selected portions of a substrate;

To provide such a process in which the configuration and position of the deposited material are accurately controllable;

To provide such a process by which high densities of particulate material are depositable;

To provide such a process in which the density of particulate material deposited is substantially uniform throughout each deposit thereof;

To provide such a process in which all of the aforementioned results are achievable simultaneously, and

To provide a process for depositing phosphor particles on selected portions of the faceplate of a cathode-ray tube, which process is capable of depositing said particles with uniform density accurately in a given configuration on said selected portions.

SUMMARY OF INVENTION

These objects are achieved, in a process comprising the steps of:

Forming on a substrate a layer of a photosensitive composition having a solubility in a given solvent which changes in response to exposure of said composition to a given radiation,

Selectively exposing a plurality of regions of said layer to said given radiation sufficiently to change substantially the solubility of said exposed regions with respect to the solubility of unexposed regions of said layer, and

Washing said layer with said given solvent sufficently to remove selectively substantially all those regions of said layer having greater solubility in said given solvent.

By forming said photosensitive layer of a composition which has distributed therethrough numerous minute particles having an equivalent spherical diameter of less than about five microns and adapted to scatter said given radia-

tion. (By "equivalent spherical diameter" is meant the particle size as measured by an electrical sensing-zone particle analyzer, e.g. a Coulter counter. Such a measuring instrument is described in the paper of O. A. Ullrich, entitled "Size Analysis of Fine Particles and Results Obtained With an Electrical Sensing-Zone Particle Analyzer," which was presented before the Instrument Society of America Conference in New York City on Sept. 26, 1960. It also is described in U.S. Pats. Nos. 2,656,508, 2,869,-078, 2,985,830 and 3,015,775.)

Typically the photosensitive composition is phosphor-free dichomatized polyvinyl alcohol and the particles include particles of calcium phosphate dibasic distributed uniformly throughout the composition.

These numerous minute particles act to produce substantially uniform illumination within the region on which the exposing radiation is incident, even though the beam of exposing radiation itself is non-uniform in intensity across its cross-section and even through reflection takes place at the substrate. This is so because the incident radiation is scattered repeatedly through very short distances by the numerous, closely spaced minute particles. Because the illumination throughout the exposed region is substantially uniform, the exposed region hardens uniformly. Hence all portions thereof are equally penetrable by phosphor particles, and all portions of the surface thereof are uniformly tacky. Therefore the cause of non-uniform densities of phosphor in the resultant dot is eliminated.

Moreover, because the exposing radiation can travel only a short distance away from one minute particle before again encountering and being scattered by another closely-adjacent minute particle, the radiation within the region undergoing exposure is constrained within a relatvely small distance of the periphery of the incident beam of exposing radiation. Hence enhanced control is obtained over the shape, size and "growth" of the exposed regions. As a result, shadowmasks having holes larger than those heretofore usable (particularly in tubes made by the slurry process) may be employed. This is desirable because it reduces heating of the shadowmask by the electron beams of the completed tube and permits increased light output for a given cathode current density therein.

In addition, the numerous minute particles adjacent the substrate trap the radiation reflected therefrom, causing it to expose more thoroughly the layer of the photosensitive material adjacent the substrate instead of causing exensive and unpredictable growth of the dot. Such more thorough exposure improves adhesion of the dot to the substrate. Because of this more efficient use of the exposing radiation within the region desired to be exposed, the desired hardness of the region is reached more quickly. Hence exposure time actually may be shortened, even though the minute particles within the layer intercept the exposing radiation.

Although the invention preferably is used as an improvement of the kind of process in which a translucent phosphor-free photosensitive layer heretofore was employed, e.g., the process described and claimed in my patent application Ser. No. 452,747, now Pat. No. 3,428,-454, the dispersion of numerous minute particles through even a phosphor-containing slurry has been found to improve the size and shape control obtainable with the slurry process by modifying the kind of light scattering which occurs within the exposed region.

DETAILED DESCRIPTION

The composition of which the photosensitive layer is formed preferably is prepared by carrying out the following steps:

(1) An aqueous suspension of particles of calcium phosphate dibasic which have equivalent spherical diameters of about 5 microns or less is prepared.

This suspension typically is prepared as follows: A cylindrical ball-milling jar having a capacity of about 1.33 gallons is half-filled with milling pebbles. Typically each pebble is spherical, initially 0.75 inch in diameter and composed of high-density alumina.

Then equal parts by weight of deionized water and calcium phosphate dibasic are placed in the jar. Typically 1500 grams of each substance is added. Then the ball-milling jar is closed tightly and is arranged horizontally on drive rollers. The jar is rolled on the rollers at between about 50 and 55 rotations per minute for seven days. During this rolling, the milling pebbles grind down the particles of calcium phosphate dibasic (which initially may have an average particle size of six microns) to particles about 95 percent of which have an equivalent spherical diameter of less than three microns and about 50 percent of which have an equivalent spherical diameter of less than about one micron.

During the milling, the viscosity of the mixture of calcium phosphate dibasic and water rises considerably, the initially watery suspension becoming pasty. The reason for this change in viscosity is not entirely clear, but the change is believed to occur as a result of hydrolysis of some of the calcium phosphate dibasic to colloidal calcium hydroxide and phosphoric acid. To obtain a more watery suspension, the jar is removed from the rollers after the seven days of rolling have been completed, and about 600 milliliters of deionized water are added to the contents thereof. The jar is closed again and is rolled for another hour at about the same angular speed as before.

At the conclusion of this rolling, the jar is opened again and its contents (excluding the milling pebbles) are poured into another cylindrical jar. Then the latter jar is rolled continually until its contents are used in formulating the photosensitive composition. This continual rolling serves to keep in suspension the finely-divided particles in the water.

(2) a Polyvinyl alcohol solution is prepared.

Twelve hundred milliliters of cold deionized water are measured into a mixing tank. While the water is being stirred, seventy grams of polyvinyl alcohol powder are added thereto. One suitable polyvinyl alcohol powder is sold by E. I. du Pont de Nemours & Co. under the trademark "Elvanol," Grade No. 52–22. This polyvinyl alcohol powder is characterized by a viscosity (as determined by the Hoeppler falling-ball method) of 21 to 25 centipoises when in a four percent aqueous solution at 25° C.

The water and polyvinyl alcohol are mixed for two hours. Then the solution is heated to a temperature of about 200° Fahrenheit and held at this temperature for about 1.5 hours. Then the heating is discontinued and the solution allowed to cool to room temperature. Then the viscosity of the solution is measured (e.g., with a Brookfield Model LVF viscometer). The viscosity of the solution is adjusted to between about 38 and 40 centipoises at a temperature of 74° C. by addition to the solution of small amounts of cold deionized water. The solution is mixed for half an hour after each such addition of deionized water and before measurement of its new viscosity.

When the solution has the appropriate viscosity, it is drained into a clean storage container. Just prior to use it is passed through a fine filter to remove any solids therein.

(3) The photosensitizing solution is prepared.

About 440 grams of ammonium dichromate crystals are measured into a clean four liter amber jug. Cold deionized water is then added to the jug to make up two liters of solution. The jug is capped and rolled for about a half hour or until all of the ammonium dischromate crystals are dissolved. The resultant solution then is filtered under suction through a pitted disc filter. The filtered solution is stored in an amber jug until needed.

(4) The photosensitive dichromated composition containing calcium phosphate dibasic particles is prepared.

An appropriate quantity of the polyvinyl alcohol solution is drawn into a clean glass jar. Then about six milliliters of the calcium phosphate dibasic suspension per

10 milliliters of the polyvinyl alcohol solution are added to the latter solution. The jar is closed and the contents thereof are rolled for at least four hours.

Then the ammonium dichromate solution is added to the contents of the jar in an amount equal to about 1.5 milliliters of ammonium dichromate solution per 100 milliliters of said contents. This addition takes place at least one hour before the time when the resultant composition is used to form the photosensitized layer on the faceplate of the tube. Prior to this use, the mixture within the jar is rolled continuously to assure homogeneous distribution of all its constituents throughout the mixture. The addition of the ammonium dichromate solution and the rolling are carried out under non-actinic (e.g., yellow) light to avoid exposure of the now-photosensitized resultant composition.

The photosensitized composition so prepared is then used to form a homogeneous photosensitive layer of film on the faceplate of the tube being fabricated. This layer or film typically is between 0.1 and 1 mil thick and for example can be applied by employing the steps described in my patent application Ser. No. 452,747, now Pat. No. 3,428,454. As described therein, an appropriate quantity of the photosensitized composition is dispensed onto the inner surface of the faceplate of the cathode-ray tube, preferably through a fine-mesh screen. Then the composition is spread by centrifugation over the entire inner surface, the excess composition being removed by aspiration at the inner corners of the faceplate. Then a gentle draft of dry warm air is passed over the so-deposited photosensitive layer to dry it and complete its solidification. Because photosensitized polyvinyl alcohol is unresponsive to yellow light, all of the foregoing steps may be carried out safely in an area illuminated with yellow light.

Thereafter the remaining steps of the process described and claimed in my patent application Ser. No. 452,747, now Pat. No. 3,428,454, are carried out to produce dots of phosphor emissive of light of a given color, e.g. green. Thus, as set forth in the above-identified patent application, after the layer is formed, selected regions thereof are exposed with ultraviolet radiation through the holes in the shadowmask which is to be used in the finished tube. Then the layer is washed with water sufficiently to remove the unexposed regions of the polyvinyl alcohol layer and soak the exposed regions thereof. Then dry phosphor powder (e.g., green-light-emissive phosphor) is projected against the soaked, exposed regions at velocities sufficiently high to embed the phosphor powder throughout these regions. As described in my patent application Ser. No. 452,747, now Pat. No. 3,428,454, such embedment typically is achieved by projecting dry particles of phosphor from one or more high-pressure airbrushes against said soaked, exposed regions. In one arrangement, the apparatus for projecting the dry phosphor particles may comprise two airbrushes (e.g. of the type manufactured by the Paasche Airbrush Co. of Chicago, Ill., comprising a Carboloy fan-spray head and needle valve) supported one above the other, means for supplying air thereto to produce two slightly overlapping high-velocity phosphor sprays, and means for moving the two airbrushes so that the phosphor particles impinge the entire area containing the soaked, exposed regions. Air having a pressure of between 60 and 70 pounds per square inch is supplied to each air gun to project the phosphor particles. For spraying a rectangular faceplate having overall dimensions of about 17 inches by 13.7 inches and supported with its long side oriented horizontally, the faceplate is arranged so that the surface to be sprayed faces the nozzles of the airbrushes and is spaced six to eight inches therefrom. The airbrushes are adjusted so that, when the high pressure compressed air is supplied to the air brushes, each brush produces a vertical fan-spray of phosphor having a width of about eight inches at the impinged surface of the faceplate and a thickness thereat of about three-quarters of an inch. The nozzles of the airbrushes are spaced from one another so that their sprays overlap by about a quarter inch at said impinged surface.

Alternatively the particles of phosphor may be projected from a single hand-held airbrush moved so as to spray the entire area containing such regions. The spraying need not be uniform over all such regions. Since the soaked, exposed regions are capable of accepting only a fixed maximum amount of phosphor, any excess phosphor is readily removable therefrom.

The dry, green-light-emissive phosphor powder to be sprayed may consist, for example, of particles of silver-activated zinc cadmium sulfide containing 40 percent by weight of cadmium. To facilitate flow of the phosphor powder through each airbrush used to spray it, those particles preferably are between about 10 and about 15 microns in extent and are coated with a small amount of silicate (e.g., a barium silicate complex). One such phosphor is manufactured by the Sylvania Electric Co. under the designation "Green Dusting Phosphor—QGX–16–1220."

After the completion of the phosphor-spraying step, the exposed regions, now loaded with phosphor particles which absorb much of the water therein, are further dried, for example by blowing dry air thereagainst for about three to five minutes at a rate of about three cubic feet of air per minute. Then substantially all phosphor powder is washed from the bared areas of the faceplate and the excess, loosely-clinging phosphor particles are washed from the surfaces of the exposed regions, e.g. by directing oscillating fan sprays of deionized water thereagainst while the faceplate is rotated slowly in a vertical plane. Then, if it is desired to deposit another array of dots containing phosphors emissive of light of a different color, the exposed regions already deposited preferably are further tanned (polymerized), e.g. by wetting the surfaces of the exposed regions with a 0.1 percent-by-weight aqueous solution of ammonium dichromate, drying such surfaces by blowing dry air thereon, and then flooding the entire surface of the faceplate with ultraviolet radiation sufficiently to photolize the ammonium dichromate taken up by the exposed regions from the latter ammonium dichromate solution.

The foregoing steps are repeated to deposit phosphor dots emissive of a second color, e.g. blue, and are repeated again to deposit phosphor dots emissive of a third color, e.g., red. As pointed out in my patent application Ser. No. 452,747, now Pat. No. 3,428,454, one suitable blue-light-emissive phosphor is silver-activated zinc sulfide, the particles of which are 10 to 15 microns in extent and are coated with a silicate to make them free-flowing. One such phosphor is sold by Sylvania Electric Co. under the designation, "Blue Dusting Phosphor, QBX–16–1320." As also pointed out in said patent application and patent, a suitable red-light-emissive phosphor is zinc cadmium sulfide containing 80 percent-by-weight of cadmium, the particles of which are 10 to 15 microns in extent and are coated with a silicate to make them free-flowing. One such phosphor is sold by the Sylvania Electric Co. under the designation, "Zinc Cadmium Sulfide Red Dusting Powder, RX–27." Another suitable red-light-emissive phosphor is yttrium vanadate activated with europium, having a particle size of about 6 to 9 microns. One such phosphor is sold by the Sylvania Electric Co. under the designation, "Rare Earth Red Dusting Phosphor, No. 1120 QRX." Because all of these steps (and other refinements) are discussed in considerable detail in my above-identified patent application, now Pat. No. 3,428,454, it is believed unnecessary to discuss them further herein.

When the above-described photosensitized composition is used to form the photosensitive layer on the faceplate of the tube, phosphor dots are obtained consistently which have a satisfactorily high density of phosphor particles

coupled with a uniform distribution of phosphor particles throughout each dot. Moreover the sizes and shapes of the dots are much more closely controllable than heretofore. In addition, crosscontamination of phosphor dots is reduced.

Although calcium phosphate dibasic is the preferred material from which the minute particles are made, other materials also have been found to be satisfactory for this purpose. For example, milk of magnesia has been found to be satisfactory when the photosensitized composition containing it is used promptly after preparation to form the photosensitive layer. This material is not preferred because it reacts relatively rapidly with the ammonium dichromate, typically rendering the photosensitized composition unsuitable for use in tube fabrication about four hours after the photosensitized composition is prepared. Ball-milled magnesium silicate and talc also have been found suitable.

The concentration of finely divided particles in the photosensitive composition is not critical. A fairly high concentration is desirable to limit to very short distances the scattering of actinic radiation. However too high a concentration will tend to dilute the color of the light emitted by the phosphor, while too low a concentration will fail to limit the scattering distances for actinic radiation sufficiently to achieve uniform illumination within the exposed regions.

The maximum effective spherical diameter of the minute particles is critical and, as aforementioned, may not exceed about five microns. When particles greater than this size are used, the dot quality deteriorates. In particular, voids often occur in the dots. There is, in practice, no critical minimum diameter for the minute particles.

Although the use of the above-described photosensitive composition has been discussed with particular reference to the process described and claimed in my patent application Ser. No. 452, 747, now Pat. No. 3,428,454, this composition also may be used with other processes in which transparent phosphor-free polyvinyl alcohol heretofore was used to form the photosensitive layer, e.g. the process described in U.S. Pat. No. 2,950,193 to P. D. Payne, Jr. Moreover even the slurry process may be improved by the addition to the slurry of numerous particles of light-scattering material having equivalent spherical diameters of five microns or less.

Although the process has been described with particular reference to photosensitized layers comprising polyvinyl alcohol, it also may be used in connection with photosensitized layers composed of other materials, e.g., gelatin, as well as in layers employed in inverse resist processes.

In addition, although the process has been described in connection with the fabrication of the image-forming screen of a color television picture tube of the shadow-mask type, it obviously can be used to fabricate color television picture tube screens of other types, e.g. those used in the Apple-type color television receivers. Moreover the process can be used to deposit non-light-emissive particulate material on a substrate in accurately determined positions, sizes and shapes.

I claim:

1. In a process for forming an image screen structure on a substrate, comprising the steps of:

forming on said substrate a layer of a photosensitive composition having a solubility in a given solvent which changes in response to exposure of said composition to a given radiation,

selectively exposing a plurality of regions of said layer to said given radiation sufficiently to change substantially the solubility of said exposed regions with respect to the solubility of unexposed regions of said layer, and

washing said layer with said given solvent sufficiently to remove selectively substantially all those regions of said layer having greater solubility in said given solvent,

the improvement which comprises forming said layer of a composition having distributed therethrough numerous particles adapted to scatter said given radiation, substantially all of said particles having equivalent spherical diameters not greater than about five microns.

2. A process according to claim 1, in which said particles include particles of calcium phosphate dibasic.

3. A process according to claim 1, in which said composition comprises photosensitized polyvinyl alcohol and said particles include particles of calcium phosphate dibasic.

4. In a process for depositing particulate solid material on a plurality of selected portions of a substrate, comprising the steps of:

forming on said substrate a layer of a photosensitive composition having a solubility in a given solvent which decreases, in response to exposure of said composition to a given radiation, by an amount directly dependent on the quantity of said given radiation incident on said composition,

selectively exposing to said radiation those regions of said layer overlying said selected portions, said exposure being suffiicent to render said regions substantially less soluble in said given solvent than the unexposed regions of said layer,

washing said layer with said given solvent sufficiently to remove selectively from said substrate the unexposed regions of said layer, and

embedding said particulate solid material in said exposed regions of said layer,

the improvement which comprises forming said layer of a composition having distributed substantially uniformly therethrough numerous particles adapted to scatter said given radiation, substantially all of said particles having equivalent spherical diameters not greater than about five microns.

5. A process according to claim 4, in which said particles include particles of calcium phosphate dibasic.

6. A process according to claim 4, in which said composition comprises dichromated polyvinyl alcohol.

7. A process according to claim 4, in which said composition comprises dichromated polyvinyl alcohol and in which said particles include particles of calcium phosphate dibasic.

8. In a process for depositing particulate solid material on a plurality of selected portions of a substrate, comprising the steps of:

forming on said substrate a layer of a photosensitive composition having a solubility in a given solvent which decreases, in response to exposure of said composition to a given radiation, by an amount directly dependent on the quantity of said given radiation incident on said composition,

selectively exposing to said radiation those regions of said layer overlying said selected portions, said exposure being sufficient to render said regions substantially less soluble in said given solvent than the the unexposed regions of said layer,

washing said layer with said given solvent sufficiently to remove selectively from said substrate the unexposed regions of said layer, and

embedding said particulate solid material in said exposed regions of said layer,

the improvement which comprises forming said layer of a composition having distributed substantially uniformly therethrough numerous particles adapted to scatter said given radiation, about 95 percent of said particles having equivalent spherical diameters of less than about three microns, about 50 percent of said particles having equivalent spherical diameters of less than about one micron, said particles including particles of calcium phosphate dibasic.

9. A process according to claim 8, in which said composition comprises dichromated polyvinyl alcohol.

10. In a process for depositing particulate solid material on selected portions of a substrate, comprising the steps of:
coating said substrate with a photosensitive layer composed of dichromated polyvinyl alcohol,
selectively exposing to actinic radiation those regions of said layer overlying said selected portions of said substrate, said exposure being sufficient to render said regions substantially less soluble in water than unexposed regions of said layer,
washing said layer with water sufficiently to soak said exposed regions of said layer and to remove from said substrate the unexposed regions of said layer,
embedding said particulate solid material throughout the thickness of each of said soaked exposed regions by projecting thereagainst, with velocities sufficient to produce such embedment, dry particles of said solid material, and
drying said exposed regions,
the improvement which comprises distributing substantially uniformly throughout said layer prior to said exposure step numerous particles adapted to scatter said actinic radiation, substantially all of said numerous particles having equivalent spherical diameters not greater than about five microns.

11. A process according to claim 10, wherein said numerous particles include particles of calcium phosphate dibasic.

12. A process according to claim 10, wherein said numerous material is a light-emissive phosphor, said substrate is a transparent screen of a display device, and said particles include particles of calcium phosphate dibasic.

13. In a process for depositing light-emissive phosphor particles on selected portions of a transparent screen of a display device, comprising the steps of:
coating said screen with a photosensitive layer composed of dichromated polyvinyl alcohol,
selectively exposing to actinic radiation those regions of said layer overlying said selected portions of said screen, said exposure being sufficient to render said regions substantially less soluble in water than unexposed regions of said layer,
washing said layer with water sufficiently to soak said exposed regions of said layer and to remove from said screen said unexposed regions of said layer,
embedding said phosphor particles throughout the thickness of each of said soaked exposed regions by projecting thereagainst, with velocities sufficient to produce such embedment, dry particles of said phosphor, and
drying said exposed regions,
the improvement which comprises distributing substantially uniformly throughout said layer prior to said exposure step numerous particles, including particles of calcium phosphate dibasic, adapted to scatter said actinic radiation, about 95 percent of said numerous particles having equivalent spherical diameters of less than about three microns and about 50 percent of said numerous particles having equivalent spherical diameters of less than about one micron.

14. In a process for forming an image screen structure on a substrate, comprising the steps of:
forming on said substrate a layer of a photosensitive composition having a solubility in a given solvent which changes in response to exposure of said composition to a given radiation,
selectively exposing a plurality of regions of said layer to said given radiation sufficiently to change substantially the solubility of said exposed regions with respect to the solubility of unexposed regions of said layer, and
washing said layer with said given solvent sufficiently to remove selectively substantially all those regions of said layer having greater solubility in said given solvent,
the improvement which comprises forming said layer of a composition having distributed therethrough numerous particles adapted to scatter said given radiation, substantially all of said particles having equivalent spherical diameters not greater than about five microns and about half of said particles having equivalent spherical diameters of less than about one micron.

15. A process according to claim 14, in which said particles include particles of calcium phosphate dibasic.

16. A process according to claim 14, in which said composition comprises photosensitized polyvinyl alcohol and said particles include particles of calcium phosphate dibasic.

17. A process according to claim 14, wherein said composition has said numerous particles distributed substantially uniformly therethrough, and said process comprises the additional step of embedding particulate solid material in those regions of said layer remaining on said substrate after said washing of said layer.

18. A process according to claim 17, in which said numerous particles include particles of calcium phosphate dibasic.

19. A process according to claim 17, in which said composition comprises dichromated polyvinyl alcohol.

20. A process according to claim 17, in which said composition comprises dichromated polyvinyl alcohol and said numerous particles include particles of calcium phosphate dibasic.

21. In a process for forming an image screen structure on a substrate, comprising the steps of:
forming on said substrate a layer of a photosensitive composition having a solubility in a given solvent which changes in response to exposure of said composition to a given radiation,
selectively exposing a plurality of regions of said layer to said given radiation sufficiently to change substantially the solubility of said exposed regions with respect to the solubility of unexposed regions of said layer, and
washing said layer with said given solvent sufficiently to remove selectively substantially all those regions of said layer having greater solubility in said given solvent,
the improvement which comprises forming said layer of a composition having distributed therethrough numerous particles adapted to scatter said given radiation, about 95 percent of said particles having equivalent spherical diameters of less than about three microns and about 50 percent of said particles having equivalent spherical diameters of less than about one micron.

22. A process according to claim 21, in which said numerous particles include particles of calcium phosphate dibasic.

23. A process according to claim 21, in which said composition comprises photosensitized polyvinyl alcohol and said numerous particles include particles of calcium phosphate dibasic.

24. A process according to claim 21, wherein said composition has said numerous particles distributed substantially uniformly therethrough and said process comprises the additional step of embedding particulate solid material in those regions of said layer remaining on said substrate after said washing of said layer.

25. A process according to claim 24, in which said composition comprises photosensitized polyvinyl alcohol.

26. In a process for depositing particulate solid material on selected portions of a substrate, comprising the steps of:
coating said substrate with a photosensitive layer composed of dichromated polyvinyl alcohol,
selectively exposing to actinic radiation those regions of said layer overlying said selected portions of said substrate, said exposure being sufficient to render said

regions substantially less soluble in water than unexposed regions of said layer,

washing said layer with water sufficiently to soak said exposed regions of said layer and to remove from said substrate the unexposed regions of said layer,

embedding said particulate solid material throughout each of said soaked exposed regions by projecting thereagainst, with velocities sufficient to produce such embedment, dry particles of said solid material, and

drying said exposed regions,

the improvement which comprises distributing substantially uniformly throughout said layer prior to said exposure step numerous particles adapted to scatter said actinic radiation, substantially all of said numerous particles having equivalent spherical diameters not greater than about five microns and about half of said numerous particles having equivalent spherical diameters of less than about one micron.

27. A process according to claim **26**, wherein said numerous particles include particles of calcium phosphate dibasic.

28. A process according to claim **26**, wherein said material is a light-emissive phosphor, said substrate is a transparent screen of a display device, and said numerous particles include particles of calicum phosphate dibasic.

29. A process according to claim **26**, wherein about 95 percent of said numerous particles in said composition have equivalent spherical diameters of less than about three mircrons.

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DAVID KLEIN, Primary Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,533,791 **Dated** October 13, 1970

Inventor(s) Louis J. Angelucci Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 54, "C" should read -- F --; line 67, "dischromate" should read -- dichromate --; line 69, "pitted" should read -- fritted --. Column 7, line 1, "10" should read -- 100 --.

Signed and sealed this 30th day of March 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents