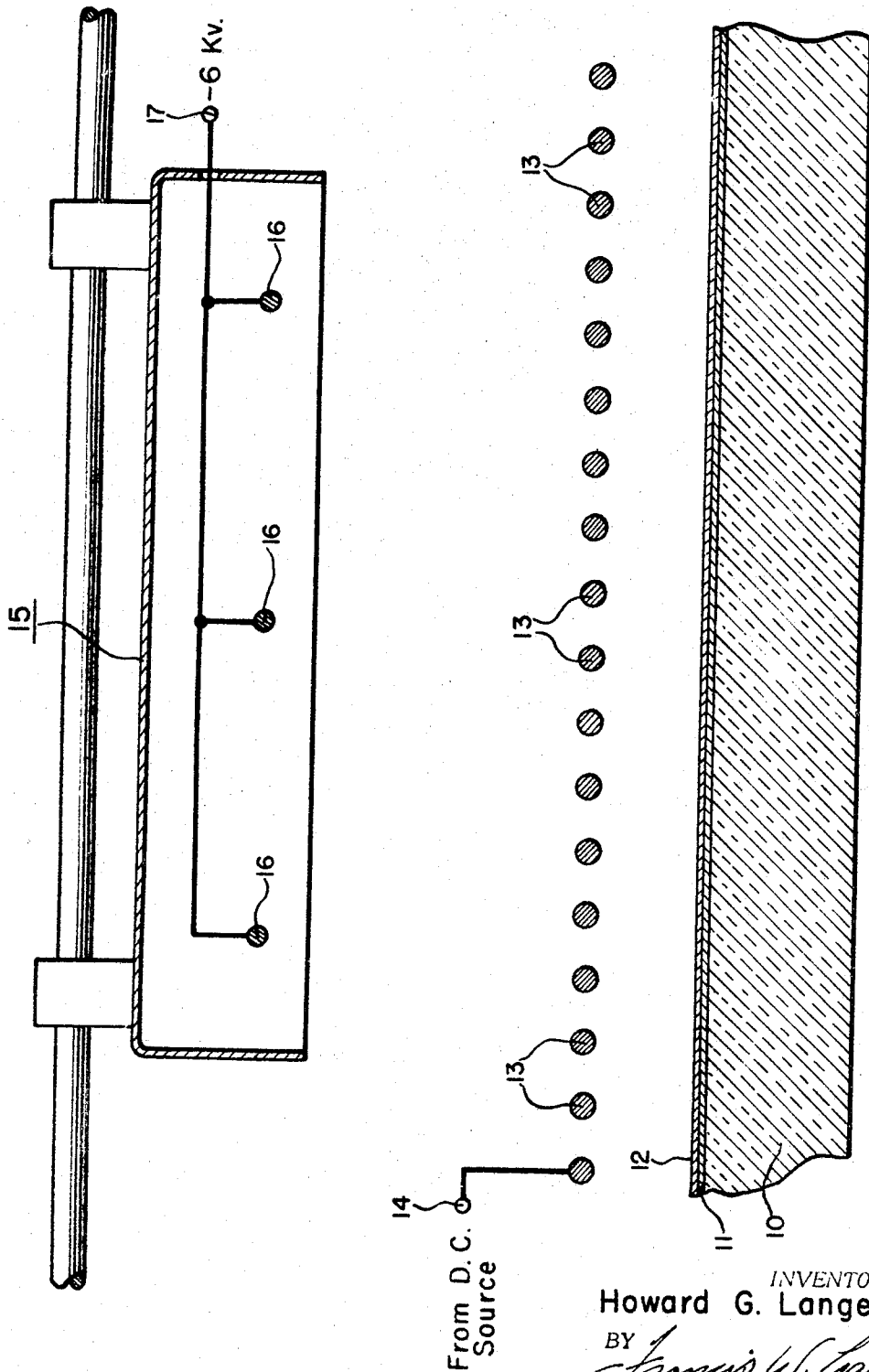


Oct. 28, 1969

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PROCESS OF ELECTROSTATICALLY SCREENING
COLOR CATHODE-RAY TUBES
Filed Aug. 20, 1965

3,475,169



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PROCESS OF ELECTROSTATICALLY SCREENING COLOR CATHODE-RAY TUBES

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Filed Aug. 20, 1965, Ser. No. 481,316

Int. Cl. G03g 7/00, 13/04, 13/22

U.S. Cl. 96—1

26 Claims

ABSTRACT OF THE DISCLOSURE

A method of electrophotographically screening the cap section of a color cathode-ray tube is disclosed. The cap is coated with a volatilizable conductive material and is then overcoated with a layer of volatilizable photoconductive material. Phosphor material is deposited by charging, exposing, and developing. A subsequent bakeout procedure removes the conductive and photoconductive layers.

The present invention is directed to the screening of color cathode-ray tubes by electrophotographic processes. It is equally beneficial in the manufacture of color tubes in which the phosphor elements are stripes, dots or other configuration arranged in an interlaced pattern on the screen.

The manufacture of color tubes generally involves a photographic process as a means for delineating the elemental areas of the screen that are to represent phosphors of one of the primary colors. For example, if the screen is of the dot triad type one photographic exposure determines the location of the dots of green phosphor; a second exposure determines the areas to be occupied by blue phosphors; and a third exposure determines the location of the red phosphors. The three exposures are obtained in known fashion by causing the light source to simulate in succession each of the three electron guns of the picture tube, assuming that the tube is of the three-gun variety. As a consequence of the several exposures, there results an interlaced pattern of dots which defines a multiplicity of dot triads over the screen surface. The three dots of each such triad are elemental areas of red, green and blue phosphors.

As color tubes are presently manufactured, a water soluble photosensitive resist is employed as a coating over the surface which receives the photographic exposure because the resist may be rendered insoluble to water by actinic light and in this way areas that represent phosphor elements are clearly distinguishable from the remaining portions of the screen. Exposure through the shadow-mask, for example, establishes a latent image of the dot areas for a particular color and the image is easily developed by washing with water to remove the resist from all areas other than those that are to represent the color being processed. This arrangement has yielded acceptable results but the exposure involves a very substantial amount of energy and takes a rather long time to create the latent image. If the image could be created and developed in shorter time and in a process which involves less energy and therefore a lower operating temperature during exposure, it certainly would be a desirable improvement in the processing of the tube.

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The present invention is directed to that end and accomplishes its objective by the application of electrophotographic techniques to the processing of color cathode-ray tubes. In addition to very substantially reducing the processing time, the electrophotographic approach has other distinct advantages especially in the production of what has come to be known as "black surrounds." The black surround is a material deposited to fill the spaces between the phosphor elements and tinted if necessary to present a border or surround that is darker than the de-energized color of the phosphor elements for the purpose of improving contrast by reducing reflectance. This has the added benefit that the face panel of the tube may be more transmissive than heretofore because it is not necessary to rely as heavily on filtering by means of the face panel to improve contrast and, consequently, the brightness of the tube is enhanced.

Accordingly, it is an object of the invention to provide an improved process for forming a screen of a multicolor cathode-ray tube.

It is a particular object of the invention to form the screen of a multicolor cathode-ray tube through the use of electrophotographic procedures.

It is another particular object of the invention to provide an improved process of making color tube screens featuring black surrounds.

Yet another object of the invention is to provide a process for screening a barrier type color tube employing the barrier element in determining the color phosphor images.

A process of electrophotographically screening the image area of a color cathode-ray tube in accordance with the invention comprises applying over the image area a conductive layer and a superposed photoconductive layer preferably formed of a resin. A latent charge image is established on the photoconductive layer and then a developer is applied over the image area. The developer includes phosphor particles of a given color as well as a binder in a carrier liquid. Preferably, the binder is formed of the same resin as that included in the photoconductive layer and this resin encapsulates the phosphor particles. The application of the developer selectively deposits phosphor particles to develop the latent image and thereafter the excess of developer is removed and the image dried.

For a three-color screen this same general process is carried out three times, once for each of the three colors, except that the conductive and photoconductive layers are laid down only once. Each color image is dried after it has been formed and when all three have been developed, they are fixed in a common fixing treatment which preferably may be accomplished by the use of methylene chloride vapor.

A three-color screen formed in this fashion may still be subjected to a charge and it will be found that only the areas of the photoconductive layer which interleave the color images do, in fact, accept a charge. Accordingly, a developer including a surround material, polarized for direct imaging and applied to the image area, results in the formation of black surround for enhancing contrast.

In accordance with one aspect of the invention the conductive substrate includes as an ingredient a controlled amount of a humectant so that the surface resistivity of the substrate may be controlled.

In accordance with another aspect of the invention, the screening process features establishing a charge on the photoconductive layer while the barrier element is in place and, preferably, having that element participate in determining the nature of the charge that is established. For example, where the barrier is a grid of parallel conductors, it may be utilized to establish lens fields to the end that the charge image takes the form of parallel stripes disposed over the image area.

Electrophotographic processes of the type under consideration have been known to the printing art in which reproductions are made by what is generally referred to as electrostatic printing. In such a process, a backing or support is coated with a layer of a photoconductive insulating material which may for example, be white zinc oxide dispersed in a carrier or film forming vehicle or binder such as a silicone resin. This layer receives a uniform electrostatic charge by scanning the surface with a corona type charging device. Thereafter a light image is focused on the photoconductive surface to selectively discharge elemental areas thereof in accordance with the intensity of the incident light. That is to say, the areas subjected to maximum light are most completely discharged while those areas that do not receive any quantity of light retain most of their charge and accordingly, the light image is converted into an electrostatic image on the photoconductor. The electrostatic image is developed by applying to the surface of the photoconductor a developer which may comprise a suitably charged toner. If the charge of the toner is of opposite polarity to the charge of the photoconductor the toner is attracted directly to those elemental areas of the photoconductor which have retained a charge but it is not attracted to those areas that have been discharged under the influence of the light image. In this manner the electrostatic image is converted into a visible image which may be fixed by heat or through a suitable fixing agent or, alternatively the visible image may be transferred in known fashion to another surface.

While a process of this general type is in commercial use for document reproduction, it presents formidable problems when employed in the manufacture of color cathode-ray tubes. In the material which follows there is described techniques for making possible its utilization in the screening of such tubes.

Color cathode-ray tubes have a two-piece envelope including a screen or cap section and a companion funnel or cone section. The cap may be likened to a flanged dish and it may have any desirable cross-section but is usually round or rectangular. The cone has the same cross-sectional configuration as the cap and is dimensioned so that its large end may fit precisely with the free edge or the flange of the cap section to facilitate their integration by frit sealing. The opposite or small end of the cone accommodates the neck of the tube which houses the electron guns for generating scanning electron beams. This application is addressed to screening and therefore the remaining description will be confined to processing the cap section in order to establish its tri-color screen.

The cap section, having first been made chemically clean is provided with a conductive layer which has a surface resistivity less than 10^{10} ohms/sq. unit and preferably less than 10^8 ohms/sq. unit; the lower the resistivity the better. It is required that the material of the conductive layer should not be dissolved or otherwise disintegrated by the subsequent processing steps such as the application of the photoconductive layer developer liquids or film solvents and it is further required that the material constituting the conductive film have no adverse effects in the operation of the tube. For example it must not constitute a gaseous source and it must not poison or otherwise impair the efficiency of the phosphors which ultimately serve as the screen of the tube. Finally the film should serve as a temporary backing for the photo-

conductive layer and be capable of removal after its function has been completed unless its presence has no adverse effect on the operation of the tube as would be the case if NESA glass were used as the conductive layer. A preferred material is an organic conductor comprising a humectant in a water soluble resin serving as a binder. The humectant retains water in the resin in a controllable amount to attain the conductivity required of the foundation layer for electrophotography and this layer must also have sufficient mechanical strength to serve as a base for a subsequently applied photoconductive layer. An acceptable humectant is ethylene glycol which is especially attractive in that the surface resistivity of the film of this humectant and a suitable resin such as polyvinyl alcohol is dependent upon humidity and may be controlled to a preselected value within a broad range.

A suitable formulation for the conductive coating is as follows:

EXAMPLE 1

	ML.
13.2% solution of polyvinyl alcohol in water (commercially available as Du Pont 52-22 "Elvanol")	40
Ethylene glycol	2
Water	20

A quantity of this material is spin coated over the screen panel of the cathode-ray tube in process at a speed of about 200 r.p.m. to apply a uniform coating of approximately 0.01" thickness over the entire screen surface. At a relative humidity of 47% and an ambient temperature of 72°F. the surface resistivity of the coating is about 3×10^8 ohms per square unit.

Other suitable humectants include ammonium chloride and ammonium acetate. Other useful resins include polyvinyl pyrrolidone a copolymer of methyl vinyl ether and maleic anhydride which is supplied under the trade name Gantrez AN-139 and AN-169 by General Aniline & Film Corporation. One may also use a styrene-maleic anhydride copolymer the ammonium salt of polyacrylic acid water soluble polyesters such as those formed from trimellitic anhydride and a glycol low molecular weight alkyds containing a high proportion of polar groups or, in general, water soluble polymers.

Having established a suitable conductive layer on the screen surface, as explained, the next step is the formation of a superposed organic photoconductive layer or substrate. For this purpose one may employ polyvinyl carbazole sensitized with anthraquinone and benzoic acid. A suitable formulation is as follows:

EXAMPLE 2

650 ml. of a saturated solution of anthraquinone in monochlorobenzene	
65 g. polyvinyl carbazole	
1 g. benzoic acid	

The photoconductive coating may be applied by spinning, flowing, spraying or the like and the required viscosity may be obtained by adding controlled amounts of monochlorobenzene. The coating is then dried either by air drying or through the use of infrared energy. It is essential, however, that the drying be carried out carefully for the reason that excessive drying tends to reduce the moisture content of the underlying conductive layer which may adversely affect its surface resistivity.

A photoconductive layer of the foregoing formulation tends to be hard or brittle and may be made more compliant by the addition of a plasticizer. While the plasticizer is not an essential ingredient, it is desirable in order to preclude cracking of the photoconductive layer. To that end there may be added to the formulation of Example 2, 65 g. of Piccolastic A-75 (supplied by Pennsylvania Industrial Chemical Corporation). Another suitable plasticizer is Piccoumaron 410-L (furnished by the same source).

The photoconductive surface may be charged by means of a corona discharge device of conventional design comprising a grid of wires and a ground plane with a high D.C. voltage connected therebetween. The voltage is of the order of 6 kilovolts but must be high enough to create a corona discharge around the wires. The polarity of the discharge is determined by the polarity of the developer to be employed and the type image desired, that is, whether a direct or a reverse image is to be developed. For a direct image the polarity of the charge on the photoconductor is opposite the polarity of the charge of the developer in order that the developer may be directly attracted to the charged areas of the photoconductive layer. Where the charges of the photoconductor and the developer are of the same polarity, they have a repelling effect so that the developer deposits in the discharged elemental areas of the photoconductor. This is known as reverse imaging.

The application of electrophotography to the screening of color cathode-ray tubes offers the distinct advantage that the parallax barrier employed for color selection in the operation of the tube may serve as the ion generator during screening. This is especially true for tubes having phosphor elements in the form of narrow elongated stripes and a wire grid positioned adjacent the screen for color selection. Utilizing the grid as the ion generator simplifies processing because the grid may serve both in charging and exposing the photoconductor and obviates the need for removing the charging apparatus between photographic exposures. Moreover, since the processing fluids may be flowed into the screen panel and poured off after accomplishing their purpose, the grid may remain in place during most of the screening operation.

It is not necessary to employ the parallax element as the ion source as described. If desired, the parallax element may be secured in position within the screen panel and a separate ionizing source may be used. The ionizing source scans the area of the parallax element and ions discharged therefrom reach the photoconductor by passing through the holes or openings of the parallax element. A representative arrangement for the grid type parallax tube is shown in the figure.

In this figure, the screen panel is designated 10 and layers 11, 12 superposed thereon are the conductive and photoconductive coatings respectively. The grid conductors 13 are parallel to one another and receive a D.C. potential from a source (not shown) connected to a common input terminal 14. An ionizing device 15 is positioned above grid 13 and has a similar grid of conductors 16 arranged in parallel to grid wires 13 but having a greater spacing as indicated. The grids 13 and 16 may have substantially the same length but grid 16 is smaller in width than grid 13 and may scan the screen by being reciprocated across grid 13 although being at all times spaced therefrom. Grid 16 is enclosed within a grounded housing and its conductors connect with a common input terminal 17 to which another high voltage source (not shown) is coupled. The voltage applied to grid 16 is high enough to establish a corona discharge as a result of which an ion cloud is formed in the space between grids 13, 16 and a sufficient number of ions are able to reach photoconductive layer 12 by passing between the conductors of grid 13. Scanning of grid 13 by source 15 tends to charge the entire surface of the photoconductor. However, if the potential of grid conductor 13 is the same polarity as the ionic discharge and is of constant value, there will be a focusing effect so that elemental portions of the photoconductor that are shadowed by grid wire 13 tend to receive a smaller charge than those portions of the photoconductor which are between these shadowed areas. This charge gradient may be minimized and the photoconductive layer given an approximately uniform charge by varying the potential of grid wires 16 within a range from 0 to several thousand, up to the voltage of ion source 15, volts at a rate that is very high compared

to the scanning rate of ionizing source 15. For example, the potential of grid 16 may be varied between 0 and 1000 volts at a 60 cycle rate.

There is also a danger that a high current density through the photoconductive layer may destroy parts of the layer and result in a nonuniform distribution of charge thereon. This may be avoided by a modification of the excitation circuit of the corona unit to include a D.C. source and a pulse source arranged in series with the conductors of the corona unit. The D.C. source may have a value of 2 kilovolts and the pulse may have an amplitude of 4 kilovolts and a repetition rate of 60 pulses per second, derived from a 60 cycle A.C. supply driving a high voltage pulse generator.

Where the tube under process is of the type in which color selection is achieved by deflection of the scanning beam under the influence of a potential pattern established on a grid of parallel wires, added flexibility is achieved by charging the photoconductive layer with the grid in situ. In such a case, the alternate or odd-numbered conductors of the grid are included in one excitation circuit while the intermediate or even-numbered conductors are included in another excitation circuit. This enables any conductor pair, that is, an odd-numbered and the adjacent even-numbered conductor, to have a controllable relative potential. For example, they may instantaneously be at the same potential or one may be selectively positive or negative relative to the other. Since the ion cloud employed in charging the photoconductive layer is of one sign or is unipolar, control of the potential of the conductor pairs constituting the grid results in focusing of the ions as they penetrate and pass through the field of the grid. The focusing action may be employed to accomplish a desired localizing of the charge on the photoconductor.

By way of illustration, the odd-numbered conductors may be maintained at a fixed positive potential relative to the even-numbered conductors during the charging of the photoconductor. If the ions have negative polarity, they are deflected toward the odd-numbered conductors in an amount determined by the potential difference of the conductor pairs and the strength of the focusing field they establish. Adjustment of the focus field enables the resulting charge pattern on the photoconductive layer to comprise a series of parallel stripes located, if desired, on portions of the layer that are shadowed by the grid conductors and not readily reached by actinic energy to which the layer may be exposed through the barrier or grid. Since the charge pattern is a discrete series of parallel stripes, it may be developed, by means of developing techniques to be described hereafter, to provide the red, green or blue phosphor lines of a line-type screen.

In similar fashion but with the relative potential of the conductor pairs suitably modified, the next charging of the photoconductive layer may develop stripes contiguous to those of the first series but now serving as the location of phosphor deposits for a second of the primary colors. A third processing cycle with a lens having an opposite effect to the first-described charging cycle locates the areas for the deposit of the third phosphor to complete the screen.

Of course, the focusing may not have as sharply defined boundaries for the phosphor stripes as desired but this may be improved by a supplementing exposure of the photoconductive layer optically. For example, after each pattern of charged strips has been created, the layer may be exposed by light through the grid, with or without an auxiliary line-type mask, to the end that both boundaries of each strip are sharpened by exposure whereas the stripes themselves are otherwise not exposed. Since the portions of the photoconductive layer between the charged stripes have not been charged, it is immaterial whether they be exposed or not.

Use of the conductive grid to create lens fields for determining the charge pattern on the photoconductive

layer permits screen patterns that are exceedingly difficult to achieve by means of optical exposures. For example, by appropriate lens potentials applied to the grid conductors it is relatively easy to obtain a screen sequence of red, blue, red, green, red, blue, etc., stripes instead of the sequence red, blue, green, red, blue, green, etc. However, the first-described sequence is not easily produced in an optical exposure arrangement. It entails the use of extra optical blocks in the path of the exposing light.

If, instead of this technique of selective charging, the whole surface of the photoconductor is uniformly charged, the next process step is to expose the charged photoconductive layer and create a latent charge image representing the distribution throughout the screen of those elemental areas to be devoted to a first one of the color phosphors required for the tube. Experience has proved that optimum results in screening color tubes are obtained by exposing the screen through the parallax element to be included in the tube under process whether that element be an aperture mask or a line grid. Accordingly, the subassembly of the parallax element installed in position within the cap of the tube is placed in an exposure chamber or lighthouse so that the photoconductor may be exposed through the parallax device by energy of a wavelength to which the photoconductor responds. Where polyvinyl carbazole is used in forming the photoconductive layer, exposure may be with visible light and if polyvinyl alcohol photoresist is used, exposure may be with ultraviolet or green light. A distinct advantage in electrophotography in contrast with slurry photochemical hardening, for example, is in the time and energy required for exposure. In electrophotographic processes the exposure may be accomplished in a matter of seconds with a lamp of only 20 or 25 watts whereas the usual slurry process requires from 15 to 20 minutes exposure time with a mercury vapor lamp of at least one kilowatt.

Aside from the extreme differences in the time and energy required, the exposure step is basically the same as that of the well known photoresist screening methods. More particularly, the exposing light source is positioned to simulate the center of deflection of the electron gun that is to energize the phosphor elements for the specific color instantaneously being applied and a correcting lens is interposed in the optical system to compensate for possible errors of registration of the beam relative to the phosphor elements. A full discussion of such an optical correcting lens is contained in Patent 3,003,874, issued Oct. 10, 1961, in the name of Sam H. Kaplan. For convenience, it will be assumed that the first exposure is for the green phosphor and the light source is, therefore, positioned to simulate the green electron gun of the tube.

Where direct imaging is contemplated, it is convenient when exposing through a grid type barrier to have the grid conductors shadow the areas on which the phosphor is to be deposited, that is to say, the areas that are not to be discharged by the exposure. It is just as expedient to expose through the aperture mask of the dot triad type shadow mask tube. In this case, however, the source of actinic energy takes the form of a ring and the geometry of the exposure setup permits controlling the diameter of portions of the photoconductive layer upon which no exposing energy falls. Accordingly, the conditions for a direct, as distinguished from a reverse, latent image may be established for either type color tube.

The portions of the photoconductive layer upon which actinic light impinges are discharged, that is to say, these areas of the photoconductor lose the charge they had previously been given whereas the other areas of that layer which are shadowed by the parallax barrier and shielded from the exposing light, retain their charge condition. As a consequence of the exposure, there is established on the photoconductive layer a latent charge image

of the elemental areas of the screen that are to be assigned to green. The next step is the development of that image using green phosphor as a component of the developer.

In developing the latent image, whether it be for the first or for succeeding phosphors that are to be applied, it is necessary to insure that the developing step does not interfere with or deteriorate previously or subsequently developed images. A variety of approaches are available to meet these requirements.

One acceptable developer is a phosphor suspended with a photoconductor in a suitable carrier having a resin binder in solution. A representative formulation is:

EXAMPLE 3

Freon	-----	ml.	100
Acryloid resin (B-66 Rohm & Haas)	-----	g.	1
Anthracene, finely powdered	-----	g.	1
Phosphor	-----	g.	1

Preferably, a surfactant to be considered more particularly hereafter is added to facilitate surface charging the phosphor particles so that they are strongly attracted to the charged elemental areas of the screen constituting the latent image to be developed, assuming for convenience, that the process employs direct imaging although it is entirely feasible to use reverse imaging if desired.

A measured quantity of the developer is poured into the screen cap, swirled or swished about to develop the latent image and then poured off. Alternatively, the tube cap may be dipped into a bath of the developer. The toner of the developing solution, that is to say the green phosphor, is influenced by the electrostatic forces of the charged areas and as the developer is swirled about, and the excess poured out of the cap, the toner adheres essentially only to the charged areas. The cap is then permitted to dry and as the carrier liquid of the developer evaporates the resin ingredient fixes the phosphor deposits in position. If the adherence is inadequate or if the developer solution does not include a binder, the image or phosphor deposits may be treated with a fixing agent of the following formulation:

EXAMPLE 4

Freon	-----	ml.	100
Acryloid (B-66)	-----	g.	1
Anthracene	-----	g.	1

The developed image is washed with the fix which, in this case, has a photoconductive ingredient (anthracene) so that the screen has a photoconductive layer that may be charged and exposed in developing another latent image corresponding to another one of the three color phosphors. Of course, the developer for the second exposure will contain this other phosphor as an ingredient.

In preparing and/or using the developer for the second latent image, care must be exercised that the carrier liquid does not dissolve the binder of the first developer or the image formed by the first phosphor may be impaired. This precaution may be satisfied by using a carrier liquid in the second developer that is not a solvent for the photoconductive binder or one may employ the same carrier liquid so long as the photoconductive binder dissolves therein at a very slow rate. Where the photoconductor requires a long time to go into solution, and this is true of the formulation of Example 4, the second image may be developed without materially affecting the first one.

Another formulation for the fixing agent is Example 5:

EXAMPLE 5

Freon	-----	ml.	100
Vinyl carbazole	-----	g.	1
Acryloid (B-66)	-----	g.	1

Such a fixing solution is similar to that of Example 4 and is used in like manner. They differ in that the vinyl carbazole is soluble in Freon and hence in its solution in Example 5 whereas the photoconductive ingredient of Example 4 is essentially in suspension because of its very limited solubility.

Another modification of the developing step makes use of a developer having a resin ingredient which, after serving its purpose of developing the latent image, is rendered insoluble in order that the same liquid may be used in treating each of the three color images without suffering impairment from the use of the carrier in previously developed images. A suitable formulation for this approach is Example 6:

EXAMPLE 6

Freon	-----ml---	100
Vinyl carbazole	-----g---	1
Phosphor	-----g---	1
Ditert.-butyl peroxide	-----mg---	1

The vinyl carbazole is a monomer and is in solution in the carrier liquid. After the latent image has been developed, the vinyl carbazole photoconductor is polymerized by heat and rendered insoluble to Freon. In this case, the vinyl carbazole is deposited with the image and fixes it.

In accordance with another modification, the developer may include a phosphor encapsulated in a binder which is insoluble in the carrier liquid. With such a developer after the image has been developed, in generally the same manner as described in the discussion of the other illustrative developers, the residue of the developer is dumped and the carrier liquid permitted to evaporate. The phosphor may now be fixed by softening the encapsulating binder and/or the photoconductive layer with a vapor which is a solvent for the surface to be softened. If the binder or photoconductor is a thermoplastic material, it may additionally or alternatively be softened by heat. After the fixing has been accomplished, the photoconductor may be reprocessed to develop the next color image. For direct imaging, encapsulating in a photoconductive resin facilitates discharging one color image when processing a subsequent image. A formula for the encapsulation of phosphor is:

EXAMPLE 7

0.6 ml. 5% solution of Luvicon M-170 polyvinyl carbazole in methylene chloride
5.0 ml. methylene chloride
3 g. green or blue phosphor, or
1½ g. red phosphor

To this is quickly added 600 ml. of Freon while stirring rapidly. The Luvicon resin precipitates out and adheres to the phosphor particles. Again, a surfactant may be added to improve image formation. Images made from developers containing a phosphor which has been encapsulated by such a technique may be fixed with a vapor of methylene chloride.

It has been found that if the image is developed with encapsulated phosphor in accordance with Example 7 and dried by permitting the carrier liquid to evaporate, the image will consist of lightly bound phosphor particles that may be rubbed off with finger pressure but nevertheless exhibiting sufficient adherence that subsequent color images may be formed by recharging, exposing and developing without appreciable loss from the first formed image. After all color images have been developed, they may be simultaneously firmly fixed with a single treatment of methylene chloride to soften the resin encapsulation of all of the phosphors at one time. In fact, fix-

ing may be accomplished by the vapor of any solvent for the resin; other suitable fixes are monochlorobenzene and orthodichlorobenzene.

Instead of having the resin in solution as in Example 6 small particles of it may be suspended along with the phosphors in the carrier liquid to be deposited therewith in developing the latent image. If a surfactant is employed, it preferably develops the same charge on the phosphor and the resin particles so that as the developer is swished around the panel, in the case of direct image formation, both the phosphor and resin adhere to the charged areas of the photoconductive layer defining the latent image and in the case of reversal image formation both go to the discharged region. Thereafter, heat or a suitable vapor may fix both the phosphor and resin particles.

A two-step developing process may be employed in which the phosphor suspended in a first carrier liquid is applied to develop the latent image and then resin particles suspended in another carrier may be applied to the previously deposited phosphor. The phosphor concentration is to be restricted so that there is sufficient electrostatic force to retain the resin which is then fixed by heat or a vapor of a suitable solvent for the resin. Alternatively, the resin particles may be floated on the surface of the carrier liquid which bears the phosphor in suspension to the end that as the carrier is slowly poured off following developments of the image, the resin deposits on the image area.

In still another developing process, the resin is dissolved in the carrier liquid having the phosphor in suspension and then the first image is developed and the excess solution poured off. Before the carrier has evaporated, another liquid which the resin is insoluble but miscible with the carrier liquid, is washed over the screen to precipitate the resin out of solution so that it fixes the phosphor serving as a binder. The two carrier liquids, if miscible, may be mixed, that is, the resin is dissolved in a first carrier and a small quantity of the second carrier in which the resin is insoluble is added in such low concentration that precipitation of the resin does not yet occur. Preferably, the second carrier evaporates at a much slower rate than the first so that after pour off, following the developing of the latent image, the first liquid evaporates rapidly and therefore increases the concentration of the second as required to precipitate the resin out of solution. An illustrative formulation is:

EXAMPLE 8

Acryloid B-66 resin (Rohm & Haas)	-----g---	1
Freon	-----ml---	100
Odorless 450 solvent	-----ml---	5
Phosphor	-----g---	1
Petronate HL (Sonneborn Chem. and Refinery Co.)	-----g---	10-5

Reference has been made to the use of surfactants in the developer for the purpose of making clean and dense images. A surfactant is a surface active agent added into the developer to enhance a charge layer on the surfaces of the particles suspended in the carrier liquid. They may act upon the phosphor as well as the resin particles to improve their response to electrostatic forces. While the mechanism of surfactants is not entirely understood, it has been determined that they may put a charge layer on a particle, that the polarity of the charge is determined by the nature of the particle and further that they affect the effective dielectric constant of the particles. The following table lists by trade name a number of image materials, surfactants usable therewith, the charge on the photoconductor and the type image (indirect or direct)

developed. The footnote references indicate the sources of such materials:

by ultraviolet is employed in producing the image charges in applying the black surround as described.

Surfactant	Image Material	Type Image	Charge
Petronate HL ¹	Eosin B ²	I	(-)
Petronate CR ¹	Manganous Carbonate ³	I	(+)
Petronate CR	do	D	(-)
Petronate HL	Hytherm Black ⁴	I	(+)
Do	do	D	(-)
FC-95 Fluorchemical ⁵	Eosin B	I	(+)
Do	do	D	(-)
Petronate HL	Ceramic Black ⁶	I	(+)
Do	do	D	(-)
Sarkosyl "O" ⁷	Manganous Carbonate	I	(+)
Do	do	D	(-)
Raybo 6 Antisag ⁸	Blue Phosphor ⁹ 33Z 646A	I	(+)
Do	do	D	(-)
Ethofat ¹⁰	Green Phosphor ¹¹ 170 P22	I	(+)
Do	do	D	(-)

¹ Sonneborn Chemical & Refining Company.

² Allied Chemical Company.

³ Baker Chemical Company.

⁴ Patent Chemicals, Inc.

⁵ Minnesota Mining and Manufacturing.

⁶ Frank D. Davis Company.

⁷ Geigy Industrial Chemicals.

⁸ Raybo Chemical Company.

⁹ RCA.

¹⁰ Armour Industrial Chemicals.

¹¹ U.S. Radium.

After the three color images have been developed, whether they be interlaced patterns of dots or stripes, it is frequently desirable to fill the spaces between the elemental color areas with a black or dark material in order to improve the contrast of the color tube. This is a known expedient and is referred to in the art as "black surround." The electrophotographic screening process has distinct advantages in respect of black surrounds as will now be made clear.

If the screening permits the entire photoconductive layer, even those portions underlying the developed color images, to be charged the screen may then be flooded with actinic light and only the photoconductive areas between the color images will be discharged since the remaining portions will effectively be shadowed by the areas of the photoconductor which constitute the color images. The use of a developer effective to produce a reverse image and carrying a toner to serve as a black surround will then accomplish the desired result, e.g., surrounding the elementary areas of the color image with a dark material.

Another approach to the application of black surround uses a photoconductor such as polyvinyl carbazole sensitized with benzoic acid and anthraquinone which is responsive to two separate and preferably spaced portions of the energy spectrum or at least has a substantial response over a sufficiently wide portion of the spectrum as to encompass two distinctly different radiations as, for example, ultraviolet and visible light. The phosphor images may be made absorptive to one type of energy and transmissive to the other. In such a case, the phosphor images are created in any of the manners described above by the use of exposures for direct imaging with the type of energy to which the image material is transmissive. Where this is done, the areas under the previous images are discharged as well as the areas where no image element is to be developed. After all three color images shall have been produced and the photoconductive layer recharged, the entire photoconductive layer is exposed from the image side but with energy to which the image areas are absorptive. The photoconductor is now discharged except for the portions thereof which underlie the phosphor images since those portions are protected by the light absorbing properties of the color images. The result is a pattern of charged images surrounded by discharged areas. The black surround may then be deposited by reverse imaging. In practicing this method, an ultraviolet absorber such as Uvinol D-50 (supplied by General Aniline & Film Corporation) may be included in the resin of the developer and the color images may be developed by exposure with visible light. Exposure

It has been discovered that certain processing may produce color images of such character that the underlying photoconductor may be recharged whereas with other processing color images may be produced of a distinctly different character in that the photoconductor beneath them is not able to take on a recharge. This influence of the properties of the color image on the chargeability of the photoconductive layer may be taken advantage of in applying black surround.

Example 7 above pertained to resin coated phosphor and its use in establishing color images. If the color images are applied in this fashion without additional fixing treatment, they permit the areas of the photoconductive layer which they overlie to be recharged. However, if such images are fixed by methylene chloride vapor, it is found that the areas of photoconductor beneath them are now unable to acquire a charge. Accordingly, with the color images applied with encapsulated phosphors and then fixed by a single treatment with methylene chloride vapor, as described above, the entire screen surface may be subjected to recharging but now the charge will be found only in the areas to which the black surround is to be applied.

The theory underlying this discovery is not understood although it may be surmised the images fixed with methylene chloride have phosphor particles that are closer together and therefore more conductive than images that are not fixed. In short, the fixed image may be more continuous within itself and with the underlying photoconductive layer so that the charge from the corona unit tends to leak off, creating the condition of charge only in the areas to which the black surround is to be applied. The use of a developer as a vehicle to carry the black surround accomplishes the desired result. It will be observed that in this method, the black surround is deposited around the elements of the color image without any requirement of exposure in the application of the surround material.

Another method of applying the black surround contemplates that the phosphor material of the color images or some other ingredient of the color images fluoresces in response to energy of a type to which the photoconductor itself is not materially responsive and emits a radiation of a wavelength to which the photoconductor does respond. For example, a photoconductor which responds to fluorescent light may include an ultraviolet absorber and be insensitive to ultraviolet. Since phosphors themselves tend to be responsive to ultraviolet, they may be employed in conjunction with such a photoconductor to emit fluorescent light. After the color images have been formed by using energy of the type to which the photo-

conductor is responsive, the entire photoconductor layer is charged. Then, the entire screen is exposed to ultraviolet light which causes the elemental areas of the color images to be excited and emit light which discharges the photoconductive layer upon which the color images have been deposited. As a result, only the surrounding areas retain the charge and the surround material may be applied by direct imaging. This same technique can also be used for imaging a screen by the direct method where it is necessary to discharge areas under previously applied color image so that no further deposits of phosphor will occur over previously established color images.

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. The process of electrophotographically screening the cap section of a color cathode-ray tube which comprises:

applying over the surface of said cap section a layer of a volatilizable conductive material having a resistivity less than 10^{10} ohms/sq. unit;

applying over said conductive layer a layer of a volatilizable photoconductive material and drying said photoconductive layer;

establishing a substantially uniform level of charge on said photoconductive layer;

exposing said photoconductive layer with light through transparent portions of a color-selection electrode to establish a latent charge image thereon;

applying over said photoconductive layer a developer, including a carrier liquid bearing a quantity of phosphor particles of a given color in suspension, to selectively deposit said phosphor on said photoconductive layer and develop said latent image;

removing the excess of said phosphor; and subsequently baking said cap section to remove said conductive and photoconductive layers.

2. The process in accordance with claim 1 which includes developing on said photoconductive layer additional images in assigned ones of phosphor of different colors prior to baking said cap section and in which each such additional image is formed by first recharging said photoconductive layer to a substantially uniform level,

re-exposing said photoconductive layer through said color-selection electrode with the source of said light positioned to establish an additional latent charge image in nonoverlapping relation with the image previously developed on said photoconductive layer, applying over said re-exposed photoconductive layer another developer, including a carrier liquid bearing in suspension a quantity of phosphor particles of the color assigned to the image being developed, to develop said additional image, and removing the excess of said other developer.

3. The process of electrophotographically screening the cap section of a color cathode-ray tube which comprises:

applying over the image surface of said cap section a layer of a volatilizable conductive material having a resistivity less than 10^{10} ohms/sq. unit;

applying over said conductive layer a layer of a volatilizable photoconductive material and drying said photoconductive layer;

establishing a substantially uniform level of charge on said photoconductive layer;

exposing preselected elemental areas of said photoconductive layer with actinic radiation through transparent portions of a color-selection electrode to discharge such areas and establish a latent charge image on said photoconductive layer;

applying and fixing to preselected elemental areas of said photoconductive layer a quantity of phosphor particles of a given color to develop said latent image;

removing the excess of said phosphor;

and baking said cap section to remove said conductive and photoconductive layers.

4. The process in accordance with claim 3 which includes developing on said photoconductive layer one or more additional images in assigned areas of phosphors of different colors prior to baking said cap section and in which each such additional image is formed by:

recharging said photoconductive layer to a substantially uniform level,

exposing preselected elemental areas of said photoconductive layer, other than areas previously exposed in the application of a phosphor, through said color-selection electrode with the source of actinic radiation positioned to establish said additional latent charge image in non-overlapping relation with any image previously developed on said photoconductive layer, and

applying and fixing to preselected elemental areas of said photoconductive layer a quantity of an assigned one of said color phosphors to develop said additional image.

5. The process in accordance with claim 4 in which each said step of exposing said photoconductive layer establishes a latent image comprising elemental areas of said photoconductive layer that have retained their charged condition and other elemental areas that have been discharged,

and in which said phosphor particles of at least one of said latent images is applied with a charge of opposite polarity to that of said charged areas to be attracted thereto and develop a direct image on said photoconductive layer.

6. The process in accordance with claim 4 in which each said step of exposing said photoconductive layer establishes a latent image comprising elemental areas of said photoconductive layer that have retained their charged condition and other elemental areas that have been discharged,

and in which said phosphor particles of at least one of said latent images is applied with a charge of the same polarity as that of said charged areas to be repelled therefrom and develop a reverse image on said photoconductive layer.

7. The process in accordance with claim 4 in which each of said latent images is developed by applying to said photoconductive layer a developer, including a carrier fluid bearing a quantity of phosphor particles of a given color in suspension.

8. The process in accordance with claim 3 in which said conductive layer is formed of a material that includes as an ingredient thereof a controlled amount of humectant for determining the surface resistivity of said conductive layer.

9. The process, in accordance with claim 4, of electrophotographically screening the image of the cap section of a parallax-type of color cathode-ray tube in which a uniform level of charge is established on said photoconductive layer with the parallax element of said tube installed in operative position in relation to said image area;

and in which said photoconductive layer is exposed to actinic radiation with said parallax element installed in its aforesaid operative position.

10. The process in accordance with claim 9 in which a charge is established on said photoconductive layer by applying a D.C. potential to said parallax element of sufficient magnitude to effect an ionic discharge.

11. The process in accordance with claim 9 in which said parallax element is a grid of parallel conductors, and in which said photoconductive layer is charged by ener-

gizing the conductors of said grid to develop between each pair of conductors thereof a lens field for determining the distribution of charge pattern established on said photoconductive layer.

12. The process in accordance with claim 3 in which said latent image is developed by the steps of applying to said cap section a developer comprising a carrier liquid in which is suspended a particular color phosphor and in which is dissolved a binder having the property that it may be rendered insoluble in said carrier liquid, removing the excess of said developer, and treating the developer to render said binder insoluble.

13. The process in accordance with claim 12 in which said binder is a monomer or a resin of low molecular weight and including the step of heating to polymerize said resin and render it insoluble.

14. The process in accordance with claim 4 which includes depositing on the portions of said cap section surrounding the elemental areas thereof assigned to receive said different color phosphors, and prior to the baking of said cap section, an inorganic surround material having light absorbing properties and in which said surround material is deposited by establishing on said photoconductive layer a latent charge image of said portions of said cap,

and applying to said cap a developer, including a fluid in which said surround material is suspended, to selectively deposit said surround material and develop said latent image of said portions of said cap.

15. The process in accordance with claim 14 in which said surround material is deposited on said cap after said different color phosphor images have been developed.

16. The process in accordance with claim 15 in which the phosphor materials comprising said developed phosphor images are absorptive to energy of a particular wavelength and including the step of exposing said cap with energy of that wavelength to establish said latent charge image of said portions of said cap.

17. The process in accordance with claim 14 in which the entirety of said photoconductive layer, even the parts thereof underneath said developed phosphor images, is charged and in which said cap is flooded with actinic radiation, discharging the parts of said photoconductive layer not shadowed by said developed phosphor images to establish said latent charge image of said portions of said cap.

18. The process in accordance with claim 15 in which the phosphor materials of said developed phosphor images destroy the ability of so much of said photoconductive layer as they overlay to retain an electric charge, and

in which said latent charge image of said portions of said cap is developed by applying to said cap a developer including a surround material polarized for direct imaging.

19. The process in accordance with claim 18 including the step of applying a fixing material to said developed phosphor images to secure the phosphor thereof in place and having the property of effectively destroying the ability of so much of said photoconductive layer as such developed images overlay to retain an electric charge.

20. The process in accordance with claim 4 in which at least one color phosphor image is developed comprising a phosphor deposit of a distinct color phosphor which is responsive to radiation of a first wavelength to emit radiation of a second wavelength to which said photoconductive layer is responsive;

and in which in developing a succeeding color phosphor image energy of said first wavelength is projected on said cap to excite said previously developed phosphor deposit and discharge so much of said photoconductive layer as such deposit overlays.

21. The process in accordance with claim 3 in which said photoconductive material is a resin and in which said image is developed by applying over said cap a developer including a carrier liquid bearing a quantity of phosphor particles of a given color and a resin which is the same as the resin of said photoconductive layer.

22. The process in accordance with claim 21 in which the phosphor particles of said developer are encapsulated in the resin component of said developer.

23. The process in accordance with claim 4 including the step of concurrently fixing all of said developed images prior to baking said cap section.

24. The process in accordance with claim 3 in which said latent image is developed by applying to said cap a developer including a carrier liquid having phosphor particles in suspension and having a resin binder dissolved therein and in which,

the cap is washed, while the binder is in a liquid state, with a liquid in which said binder is insoluble to precipitate said binder out of solution and fix said image.

25. The process in accordance with claim 3 in which said latent image is developed by applying to said cap a developer including a first carrier liquid having phosphor particles in suspension and having a resin binder dissolved therein and further including a second carrier liquid which is miscible with said first liquid, has a much slower rate of evaporation than said first liquid and in which said binder is insoluble.

and including the step of drying said cap to increase the concentration of said second liquid and precipitate said binder out of solution.

26. The process in accordance with claim 3 in which said latent image is developed by applying to said cap a developer including a carrier liquid bearing a quantity of phosphor particles and a photoconductive resin in suspension.

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U.S. Cl. X.R.

96—1.2, 1.5; 117—17.5, 33.5, 37; 313—92