

Jan. 26, 1971

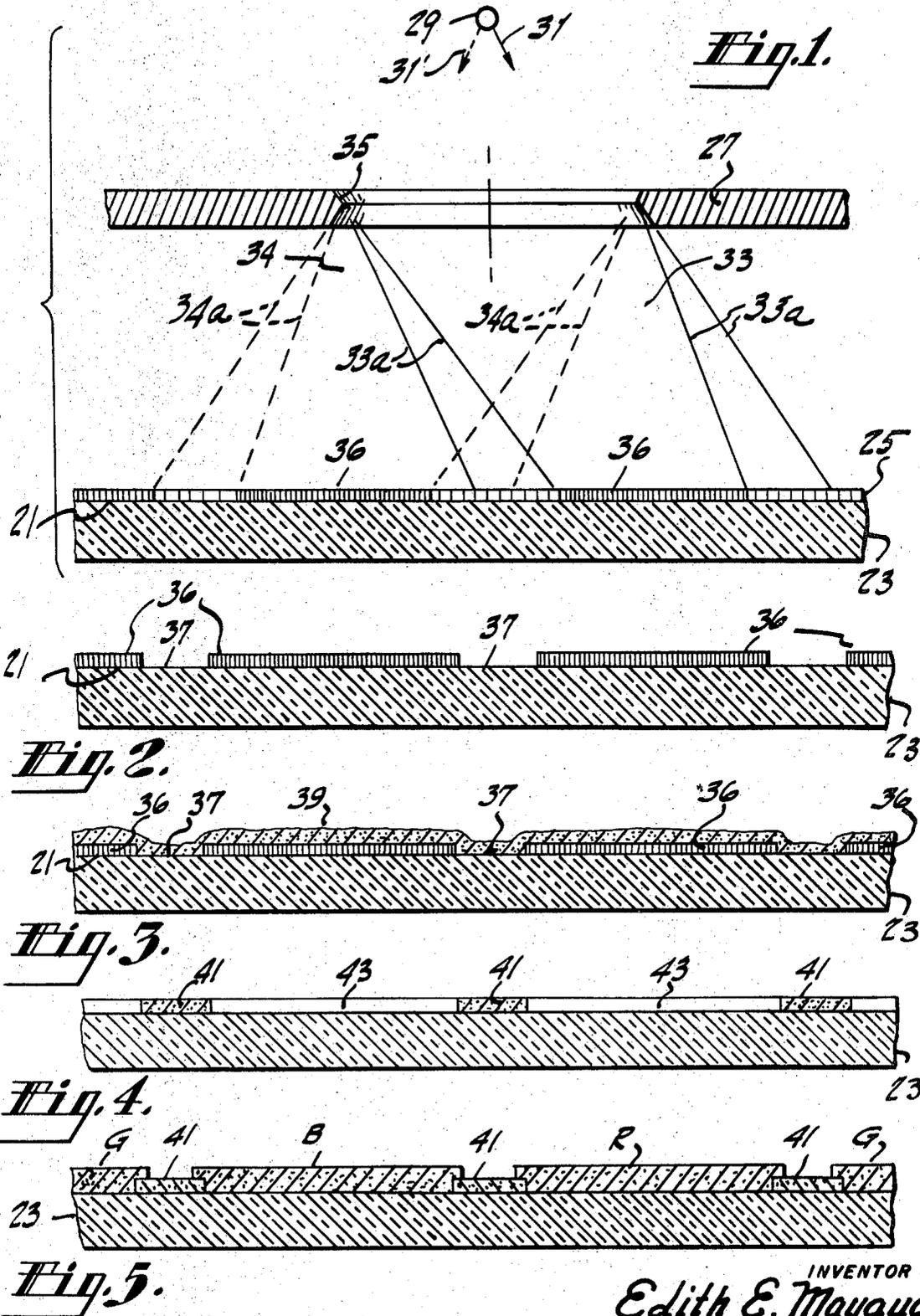
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3,558,310

METHOD FOR PRODUCING A GRAPHIC IMAGE

Filed March 29, 1967

2 Sheets-Sheet 1



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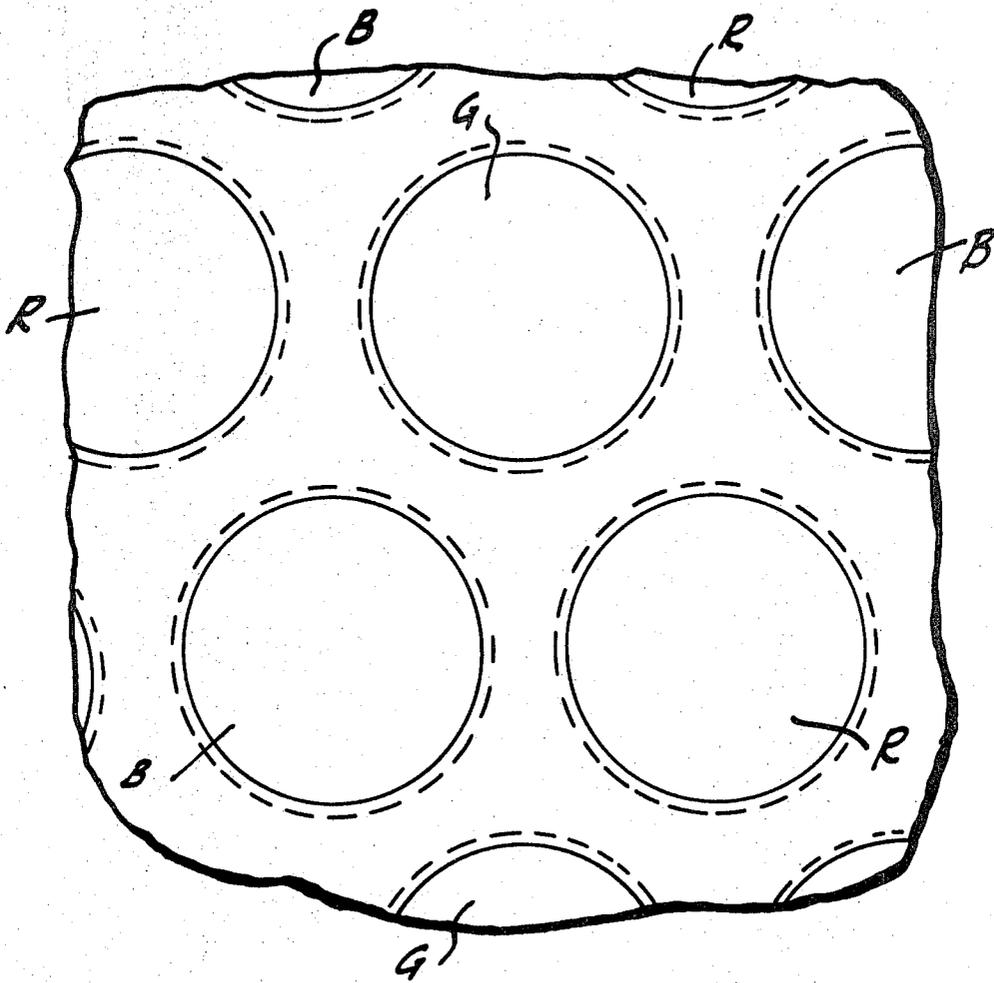


Fig. 6.

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1

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3,558,310

METHOD FOR PRODUCING A GRAPHIC IMAGE

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Filed Mar. 29, 1967, Ser. No. 626,752

Int. Cl. G03c 5/36

U.S. Cl. 96—36.1

12 Claims

SUMMARY

Generally, the novel method comprises, first, producing upon a supporting surface a stencil consisting essentially of uncoated areas of the surface and areas of the surface having adhered thereon a film consisting essentially of a polymeric material. This may be achieved photographically; for example, by coating the supporting surface with a film of a negative-acting photosensitive material, exposing the film to an image or pattern of radiant energy, and then developing the exposed coating in the usual way.

Then, the stencil is overcoated with a composition that is adherent to the uncoated areas of the supporting surface. The overcoating may include particles of a light-absorbing material, such as graphite or carbon black. The overcoating may also include a substance which enhances the adhesion of the light-absorbing material to the supporting surface. For example, colloidal silica may be included to improve the adherence of carbon black to a glass supporting surface.

Then, at least a portion of the film comprising the stencil together with the overcoating thereon is removed, while retaining the overcoating on the uncoated areas of the supporting surface, thereby producing the desired graphic image. In processes wherein the film composition consists essentially of polyvinyl alcohol, this latter step may be carried out by applying to the overcoating an aqueous solution of an oxidizing agent, such as a solution of hydrogen peroxide or sodium hypochlorite. The solution penetrates the overcoating and causes the film beneath to swell and soften. Further action by the solution causes the swelled and softened coating to degrade so that at least a portion of film comprising the stencil together with the overcoating thereover may be flushed away with water.

Some of the numerous advantages of the novel method are as follows:

First, a negative-acting photosensitive material is used to produce a positive graphic image. Thus, many commercially practical negative-acting materials become available for producing a graphic image with image reversal. Alternatively a positive-acting photosensitive material may be used to produce a negative graphic image.

Second, there are available, at present, commercially practical water-based overcoating compositions that may be used with a negative-acting material. Thus, one may provide a completely water-based processing system for making the graphic image by the novel method.

Third, the material constituting the final graphic image is not present during the photographic step. As a result, the properties of the graphic image material (pigment or dye) and of the photosensitive material do not interfere with one another, and each material may be selected independently of the other. And, the novel process does not require a compromise in the photographic speed of the photosensitive material, or in the resolution of the graphic image which is produced therewith, as in processes wherein the photosensitive material is mixed with the graphic image material.

Fourth, the graphic image is adhered directly to the supporting surface, and not by way of a light-induced change in the photosensitive material. Hence, the adherence of the image to the surface may be optimized.

Fifth, the graphic image never touches the support surface where it is protected by the photosensitive stencil, and therefore poor cleanup is prevented in areas where the graphic image material should not be deposited.

Sixth, the process is adaptable to factory operations including conveyor techniques of continuous production, both because it may use conventional manipulation procedures and because it may use only commonly available water-based chemicals.

ABSTRACT OF THE DISCLOSURE

A method for producing a graphic image upon a supporting surface. The method may be used particularly to produce a light-absorbing matrix on the faceplate of a color television picture tube. In the method, a negative-acting photoresist may be used to produce a positive graphic image; or a positive-acting photoresist may be used to produce a negative graphic image.

BACKGROUND OF THE INVENTION

Color television picture tubes which include a light-absorbing matrix as a part of the luminescent screen structure have been described previously; for example, in U.S. Pat. Nos. 2,842,697 to F. J. Bingley and 3,146,368 to J. P. Fiore et al. These patents describe color television picture tubes of the aperture mask type (also called shadow mask type) in which a light-absorbing matrix is located on the inner surface of the faceplate of the tube. In this structure, the matrix has a multiplicity of holes therein, each phosphor dot being concentric with one hole in the matrix.

In view of numerous practical problems of manufacturing it is desirable to deposit the phosphor dots and the light-absorbing matrix by a photographic process in which the aperture mask is used as a photographic master. The prior art, recognizing that there is an image reversal involved in making the light-absorbing matrix by such photographic processes, suggests using a photopolymer or photoresist of the type that is solubilized when it is irradiated with light. This type of photosensitive material is referred to herein as positive-acting because it normally produces a positive graphic image from the light image. Presently available positive-acting photosensitive materials are commercially impractical to use for this purpose because they require unreasonably long exposures, they are expensive, they have poor adherence to glass, they produce images of undesirably high contrast, and/or they require the use of inflammable non-aqueous solvents. There are, however, negative-acting photosensitive materials available which are water-based, which require reasonably short exposure times and which are otherwise commercially practical, except that they normally produce a negative graphic image. In view of such practical considerations, a desirable method for producing a graphic image is one which may be carried out entirely with water-based compositional systems, and which uses only negative-acting photosensitive materials.

It has been observed previously that when dark-colored or opaque dyes or pigments are mixed with a photosensitive material, the mixture is substantially insensitive to light. It is believed that the pigment or dye absorbs substantially all of the incident light, so that the photosensitive material is substantially unaffected by the incident light. A desirable photographic process for making a graphic image of pigment or dye is a process in which the pigment or dye is not mixed with the photosensitive material, and, therefore, does not affect the sensitivity of the photosensitive material.

Seventh, as applied to cathode ray tube manufacture, the method leaves only a relatively small residue of organic matter, if any, and this may be removed later by baking.

BRIEF DESCRIPTION OF THE DRAWINGS

The novel method is described in more detail with reference to FIGS. 1 through 5 which are fragmentary sectional views through the faceplate of a cathode ray tube for color television illustrating a sequence of steps for preparing a light-absorbing matrix on the inner surface of the faceplate by the novel method, and

FIG. 6 is a front view of a fragment of the faceplate of a picture tube for color television prepared by the method illustrated in FIGS. 1 through 5.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

FIG. 1 illustrates several of the initial steps of the novel process toward preparing photographically an adherent stencil of a polymeric material through only one hole of an aperture mask. First, the inner surface 21 of a faceplate 23 of a cathode ray tube is cleaned in the usual way and then coated with a film 25 of a clear photosensitive material. In this example, the photosensitive material is a polymer, particularly a polyvinyl alcohol containing a soluble dichromate. The photosensitive film is prepared by applying to the surface 21 a quantity of an aqueous solution comprised of about 2 weight percent polyvinyl alcohol (E. I. du Pont, Elvanol 50-42), and about 0.2% ammonium dichromate in water. The faceplate 23 is rotated and tilted so that the solution spreads evenly over the surface 21. During the latter stages of the rotation, infrared heat is applied so that the water in the solution evaporates and the film 25 is dried. The term "film" is used herein to describe a layer which is substantially free of cracks that extend through the thickness of the film.

Next, an aperture mask 27 is positioned above the film 25 and the assembly is placed in a lighthouse" (not shown). A "lighthouse" is an apparatus designed to expose the photosensitive coating on the faceplate with a pattern of ultraviolet light in the correct positions and dimensions, as is well known in the art of color picture tube making. A suitable lighthouse is described in U.S. Pat. No. 2,885,935 to D. W. Epstein et al. In this example, the mask 27 has circular apertures 35 with a diameter of approximately 11 mils and a center-to-center spacing between apertures of about 22 mils near the center of the mask. The apertures are slightly reduced in size and increased in spacing in progressing from the center toward the edge of the mask. FIG. 1 indicates schematically a small diameter light source 29 from which light emanates for exposing the film 25. The light source 29 is a Westinghouse 100 watt EM 4 projector flood lamp positioned at about 10 inches from the aperture mask. Light from the lamp is passed through a near ultraviolet (about 3650 Å.) filter and collimator (not shown). The duration of the exposure is about 45 seconds.

During the exposure, the collimated light rays, whose direction is indicated by the arrow 31, are incident upon the aperture mask 27 causing beamlets 33 of light to pass through the apertures 35 in the mask 27. The beamlets 33 which pass through the apertures 35 cause areas 36 of the film 25 to harden (i.e. becomes insoluble in water) in substantially the identical shape and size as the projected cone of light falling through the apertures 35 in the mask 27. There is a slight increase in diameter of the beamlets 33 and a slight fallout of light intensity at the margins of the beamlets, as indicated by the double lines 33a in FIG. 1. This produces a slight enlargement of the exposed areas (to about 13 mils) and a graded hardening of the film 25 at the margins of the exposed areas.

The exposure through the mask 27 is repeated three times, each time with the light rays incident at a slightly

different angle, so that the beamlets 33 harden the coating in groups of three, as in the usual method of shadow mask screen manufacture. The beamlet 34 and the margins thereof 34a indicate a second exposure of the film 25 of collimated light from a light source 29 (whose direction is indicated by the arrow 31'). Thus, at this point in the process, there are three hardened circular areas or dots 36 each about 13 mils in diameter in the film 25 for each aperture 35 in the mask 27. Each circular area has a graded hardening about 2 mils wide around its periphery.

Following exposure, the assembly is removed from the lighthouse and the mask 27 is separated from the faceplate 23. The exposed coating 25 is subjected to flushing with a forced spray of water for about 30 seconds, after which the faceplate 23 is washed with water and then drained. At this point in the process as illustrated in FIG. 2, the faceplate surface 21 carries an adherent stencil comprised of open areas 37 and dots 36 of a hardened polymeric film 25 coated on the surface 21. The dots 36 are about 11 mils in diameter. This slight reduction from the diameter (of about 13 mils) of the hardened areas results from the dissolution of the extreme edge of the circular areas which are only slightly hardened during exposure.

The stencil is now overcoated with a composition 39 comprised of light-absorbing pigment particles, as illustrated in FIG. 3. In this example, the overcoating 39 is produced by applying to the stencil a slurry containing about 4.0 weight percent of colloidal graphite in water and then drying the layer of residual material. It is desirable to include a trace of a wetting agent in the slurry in order to facilitate the spreading of the graphite slurry over the stencil. The overcoating 39 is dried thoroughly for about 1.5 minutes with the aid of infrared heat. After cooling, the overcoating 39 is well adhered both to the dots 36 and to the part of the surface 21 exposed by the open areas 37 of the stencil.

Next, the overcoating 39 is wetted with water and drained. Then, before drying, a chemically-digestive agent for the dots 36 is applied to the overcoating 39. In this example, the digestive agent is an aqueous solution containing about 35 weight percent hydrogen peroxide. If desired, this solution may be applied to the overcoating 39 as a spray under pressure. The hydrogen peroxide solution penetrates the overcoating 39 and the dots 36, causing the hardened polyvinyl alcohol of the dots 36 to swell and soften. Subsequent flushing with water removes the softened dots 36 together with the overlying portions of the overcoating 39, but leaves behind that portion of the overcoating 39 which is adhered directly to the surface 21 at the open areas 37. As illustrated in FIG. 4, the product at this point is a light-absorbing (black) matrix 41 having a multiplicity of circular holes 43 therethrough about 11 mils in diameter.

The light-absorbing (black) matrix 41 is now rinsed with water and dried for about 4 minutes with the aid of infrared heat. Then, the faceplate 23 is processed in the usual way to deposit red-emitting phosphor dots R, green-emitting phosphor dots G and blue-emitting phosphor dots B about 13 mils in diameter over the holes 41 by the usual photographic technique using the same aperture mask 27 as a photographic master in the process. It will be noted that the phosphor dots are somewhat larger than the holes 35 in the aperture mask 27. As pointed out above, the spreading of the light of the beamlets 33 causes a somewhat larger area to harden. By increasing the exposure time, the hardened areas are not substantially reduced in diameter during the subsequent rinsing steps. The completed structure is illustrated in FIGS. 5 and 6 which show the matrix 41 with the holes 43 therein and the phosphor dots R, G and B being substantially concentric therewith. A suitable process for depositing phosphor dots is described in an article entitled "Color-Television Screening by the Slurry Process" by T. A. Saulnier, Jr., in *Electrochemical Technology*, 4, 27-31 (1966).

5

The luminescent screen structure may now be processed in the usual way to apply a reflective metal layer on top of the phosphor dots and the black matrix 41. The screen structure is baked and assembled with the aperture mask 27 into a cathode ray tube in the usual way. A suitable process for filming and aluminizing is described in an article entitled "Emulsion Filming for Color Television Screens" by T. A. Saulnier, Jr. in *Electrochemical Technology*, 4, 31-34, (1966).

The particular steps described above in Example 1 may be varied within limits and still fall within the scope of the invention. Obviously, the process may be applied to producing graphic images on other supports, and for other purposes than those described in Example 1. For instance, the process may be used for producing a resist pattern upon a surface of a semiconductor body as an intermediate step in producing integrated circuits in electronics.

The photosensitive material—The preferred photosensitive material is produced by coating the substrate with a solution of polyvinyl alcohol containing a small amount of ammonium dichromate. Instead of ammonium dichromate, one may use sodium dichromate, potassium dichromate, soluble salts of metals such as iron and mercury, and also organic photosensitizers for water-based photosensitive material, such as diazo compounds.

Besides polyvinyl alcohol, other polymeric photopolymers may be used. Some suitable hydrophilic (water-based) materials which can be made photosensitive are proteins such as gelatin, albumin, fish glue, carbohydrates such as gum arabic and starch; and synthetic materials such as polyvinyl pyrrolidone, and certain acrylic acid derivatives. In general, multifunctional water-soluble polymers containing reactive groups, such as —OH, —COOH, NH_2 , —CO, singly or in combination may be used. Mixtures of these materials may also be used. Some suitable solvent-based photosensitive materials are polyvinyl methyl ketone, KPR and KMER (available from Kodak, Rochester, N.Y.) aminated polystyrene, and hydroxy esters of polyacrylates. Hydrophilic materials are preferred, at least because there are a large number of aqueous solutions that can be used in the subsequent steps of graphic image development. Solvent-based photosensitive materials are not as readily attacked by aqueous solutions. Suitable reagents for the graphic image development of solvent-based photosensitive materials are acids, bases, and commercial strippers.

It is desirable that the photosensitive material form a smooth, unbroken and uncrazed layer, since this will produce the sharpest, cleanest graphic images. To this end, it is preferred that the photosensitive material be film-forming either directly upon deposition or during a heating step subsequent to deposition. In many systems, the film-forming temperature can be tailored by adjusting the relative proportions of ingredients constituting the photosensitive material.

The resistance of the stencil to the erosive action of the graphic image developer or pattern diminution agent may be adjusted, if desired, by including in the photosensitive material a small amount of a less water-sensitive polymer. If the photosensitive material is principally a hydrophilic polymer. For example, where the photopolymer is principally polyvinyl alcohol, it is preferred to include a small amount of an acrylic polymer or copolymer. The proportion of acrylic polymer may be up to about 100% of the proportion of polyvinyl alcohol present in the coating.

The photosensitive material may be of the type which is insolubilized when exposed to energy in the form of rays of either light or electrons. Such photosensitive materials are referred to herein as negative-acting. Instead, one may use a photosensitive material of the type which is solubilized when exposed to radiant energy. This latter type of photosensitive material is referred to herein as positive-acting.

The photographic master—Any pattern form may be

6

used as a photographic master for exposing the photoresist coating. Thus, conventional silver halide images may be used either by projection or contact printing. In the case of preparing luminescent screens for cathode ray tubes, one may also use an electron beam exposure whereby the electron beam traces out the pattern by conventional scanning techniques without the use of a photographic master. In other applications, a mask may be used between the electron gun and the screen. In preparing television picture tubes of the shadow mask type, it is preferred to use the aperture mask of the tube as a photographic master for exposing the photosensitive coating. In that case, the light source is placed at three separate locations in order to produce three separate exposures on the coating, each at a different location. Thus, three holes are produced in the graphic image for each aperture in the mask. Of course, the aperture mask or other master may be used to produce only one, or two, or more than three exposures for the same coating. The shape and size of the apertures in the aperture mask is not critical.

The photoexposure—The photosensitive material is exposed to a pattern of energy rays in the range and of the type to which the photosensitive material is sensitive. Where dichromated polyvinyl alcohol is the photosensitive material, radiant energy in the form of electron beams or as light in the blue and ultraviolet range of the spectrum may be used. Where a contact master is used, one may use a flood exposure. Where the exposure is by projection of an image, a small diameter source is preferred.

Stencil development—Where a photoresist technique has been used for producing the stencil, the exposed photoresist coating is developed in the manner of the use for that material. In the case of dichromated polyvinyl alcohol, the development is carried out by flushing the surface of the coating with water or with other suitable solvent for the unexposed, still soluble resist. With other resists, the same or other solvents may be used.

Stencil diminution—This step is entirely optional in the process and is used only in the situation where it is desired to produce the same pattern as the master but that the graphic image should have smaller unprinted areas therein. This step is omitted from the process described in Example 1, but may be included if it is desired. In the case of making cathode ray tubes of the shadow mask type, the desirability of this graphic image change has been explained in the prior art. However, useful cathode ray tubes of this type can be made without any alteration in the master; that is, the light-absorbing matrix (graphic image) has substantially the identical shape as the master, but has a different pattern size. One of the advantages of novel method described herein is that graphic image size can be altered conveniently and controllably.

When stencil diminution is desired, the stencil is treated with an aqueous solution of a chemically-digestive agent. The effect of the digestive agent is to erode the edges of the coating constituting the stencil in a controlled manner. The amount of erosion (and hence the size of the printed areas in the final graphic image) is a function of the concentration of the digestive agent applied, the duration of treatment with the digestive agent, and the duration of the exposure used to produce the stencil. Since the diminution must be carefully controlled, it is preferred to use dilute solutions so that the rate of reaction which causes the diminution can be carefully controlled and so that the diminution occurs only at the edges of the stencil coating. On image stencils of hardened polyvinyl alcohol or other hardened water-soluble materials, dilute solutions of the following agents may be used: hydrogen peroxide, alkali hypochlorites and alkali perborates.

The image stencil diminution agent is chosen so as to achieve stencil diminution without impairing the adherence of the stencil to the substrate. Thus, in the case of a glass substrate, the preferred agents are acidic or neutral, since alkaline materials tend to destroy stencil adherence to glass. Extremes in pH are in general to be avoided. By

dilute is meant that type of solution whose rate of reaction is relatively slow and controllable. Thus, the exact percentage of chemically digestive agent used will vary among the agents. In the case of hydrogen peroxide, by "dilute" is meant solutions containing between 0.1 and 16 weight percent of hydrogen peroxide. The rate of stencil diminution varies inversely with the time of exposure used to produce the stencil. Overexposure of the dot may prevent diminution from taking place in a regular and well-controlled manner because overexposure may cause a hard inert cap to form the surface of the coating. Prolonged treatment with the digestive agent has little additional effect on this inert cap. Also, overdrying of the photosensitive coating (either by over-extended drying time or by using high temperatures) before exposure may produce a similar inert cap. A similar inert cap may form by overdrying the stencil. It is preferred in preparing the photosensitive coating and the stencil, to use a minimum amount of heat in drying.

Since the rate of stencil diminution with dilute oxidizing agents varies approximately inversely with the exposure used in hardening the photoresist, the intensity of the exposure is preferably fairly uniform at the center portion of the coated areas of the stencil and drops off as the edge of the image is approached. In this type of exposure, the stencil diminution progresses relatively rapidly at the outset of development since the photoresist has a minimal exposure at the edges (and therefore is less insolubilized) and then decreases in rate as diminution proceeds due to the increased exposure toward the center of the coating (and therefore is more insolubilized).

Further details and examples, including the step of dot diminution, are disclosed in U.S. application, Ser. No. 626,753, filed Mar. 29, 1967, by Edith E. Mayaud and now abandoned.

The overcoating—The overcoating may be of any material which is adherent to the support surface. The overcoating may include a pigment or dye. Where it is desired to produce a light-absorbing matrix for a cathode ray tube, it is preferred to include in the overcoating a relatively high loading of a dark pigment. The pigment is preferably elemental carbon in the form of carbon black, acetylene black, or graphite. Other black pigments that may be used are silver sulfide, iron oxide, lead sulfide, ferrites, and manganese dioxide. Broadly speaking, the novel method may be used to deposit black, white or colored pigments, resins, and dyes, where such are desired in the graphic image.

The overcoating must make a bond to the supporting surface that will resist the subsequent processing such as removing the image stencil and depositing the phosphor dots. With some materials, such as some commercially available dispersions of graphite in water, the graphite upon drying makes a bond to a glass faceplate which is adequate. With other materials, it may be necessary to include a small amount of a binder in the overcoating such that the dry overcoating develops a bond to the supporting surface through the use of the binder. Of the various inorganic binders tested, a colloidal silica was the most satisfactory binder for lamp black and acetylene black. For example, about 10% of a colloidal silica with respect to the percent pigment present also produces a strong bond to the glass faceplate, especially where a small amount of ammonium dichromate is also present. Besides colloidal silica, alkali silicates may also be used as the binder. In some cases it may not be desirable to include a pigment in the overcoating. Instead, the overcoating may consist of a clear or dyed material which one may look upon as substantially entirely binder.

Where a pigment is used for the purpose of making a light-absorbing matrix for a picture tube of the shadow mask type, the pigment must be deposited in sufficient density to develop the necessary opacity for this purpose. In the case of acetylene black and lamp black, the pigment should be deposited in a weight of 0.2 to 2.0 mg./cm.² of

surface area and, preferably, about 1.0 mg./cm.² or more in order that sufficient thickness remain after tube processing. Where graphite or other pigments are used, slightly lower weights are required for achieving the same opacity in the final graphic image.

The overcoating should also be permeable to and substantially unaffected by the graphic image developer, which must swell or erode or dissolve at least a part of the image stencil. Where the overcoating is entirely particles, it is necessarily permeable. Where the overcoating is partly or entirely a binder, the overcoating may be permeable by nature or may be made permeable by crazing the overcoating. The bond between the supporting surface and the overcoating is preferably an inorganic one, and which is not substantially attacked by the graphic image developer. When the overcoating-supporting surface bond is both inert to the attack of the graphic image developer, and is adherent to the supporting surface, it is possible to develop the graphic image after softening with a high pressure spray of water, without any alteration of the pattern due to localized over-development. If desired, appreciable amounts of organic material may be incorporated in the overcoating, provided that the overcoating is not so attacked by the graphic image developer that there is an appreciable loss of adherence to the supporting surface.

Graphic image development—Any substance that dissolves or degrades the polymeric material of the stencil into soluble, partially-soluble, or volatile fragments and leaves the overcoating substantially unattacked may be used for developing the graphic image. Thus, in one embodiment the graphic image may be developed by baking the overcoating in an oxygen-containing atmosphere so that the polymer of the stencil is volatilized. Then, the overcoating is washed as with water. This causes the overlying overcoating to be flushed away in the areas which, previous to bake out, had the hardened areas of the image stencil on them, but leaves behind overcoating in areas not previously covered by the hardened areas of the image stencil.

The preferred method for graphic image development is to apply to the overcoating an aqueous solution of an oxidizing agent in a concentration sufficiently high such that rapid penetration of the overcoating and softening of the stencil occurs. In the case of stencils of hardened polyvinyl alcohol, the stencil softens rapidly with aqueous hydrogen peroxide solutions having a concentration of 35% or higher. Instead of hydrogen peroxide solutions, aqueous solutions of the following may also be used: nitric acid, sodium peroxide, or other alkali peroxides, perchloric acid or alkali perchlorates, hydrofluoric acid, alkali hypochlorites, peracetic acid, alkali borates, alkali perborates, sodium hydroxides and certain enzymes. The graphic image developer solution is chosen so that it will not substantially decrease the adherence of the matrix overcoating to the substrate.

The time and temperature for carrying out the graphic image development is not critical, especially in view of the fact that it depends only on the removal of the polymeric material of the stencil. However, too fast a development may result in disruption of the overcoating, and too slow a development may result in the weakening of the bond between the overcoating and the support surface. Hence, in each case, the optimum time and temperature for image development is empirically determined.

Image development may also be carried out with non-aqueous reagents and mixtures of solvents and water-based reagents.

Example 2

Follow the procedure described in Example 1 except use for the overcoating composition an aqueous suspension containing 10% acetylene black, 1% colloidal silica, 0.6% ammonium dichromate, 0.01% surfactant; and carry out the graphic image development using 35%

hydrogen peroxide solution in water. Allow the peroxide solution to remain on the overcoating for a few minutes and then pour off the solution and flush the overcoating with water for about 30 seconds.

Example 3

Clean the inner surface of the faceplate of a cathode ray tube in the usual way and then coat thereon a thin layer comprised of 0.2% polyvinyl alcohol dissolved in water. Then, coat and dry the inner surface with a mixture of 1% polyvinyl alcohol, 1% methyl methacrylate resin emulsion (Rhom and Haas Code B 85, Philadelphia, Pa.) and 0.1% ammonium dichromate in water. The layer is produced by slurry coating and drying as explained in Example 1. Then, expose the sensitized layer through an aperture mask and develop the exposed layer as described in Example 1 to produce a stencil. Next, apply an aqueous suspension containing 4% colloidal graphite to the stencil and dry for 1.5 minutes with heat to produce an overcoating. Wet the overcoating with water, drain, and immediately apply an aqueous solution containing 35% by weight hydrogen peroxide adjusted to a pH of 6.5 with sodium hydroxide. Allow to stand for about 2 minutes. Then drain the hydrogen peroxide solution and develop the graphic image by flushing with water for about 30 seconds. Then dry the developed graphic image and proceed with luminescent screen processing.

Example 4

Clean the inner surface of the faceplate of a cathode ray tube in the usual way and then coat thereon a layer of an acrylic coating (for example EXM 65051, available from the Glidden Co., Cleveland, Ohio) and cure the layer 20 minutes at 175° C. Then apply a coat of 3% bone gelatin containing 0.9% ammonium dichromate dissolved in water by slurry coating and drying as explained in Example 1. Then expose the sensitized coating through an aperture mask and, using warm water, develop the exposed layer as described in Example 1 to produce a stencil. Next, apply an aqueous suspension containing 2% colloidal graphite in 1 part of water to 1 part alcohol to the stencil by spraying it. Allow the overcoating to dry. Wet the overcoating with water, drain, and immediately apply an aqueous solution containing 35% by weight hydrogen peroxide adjusted to a pH of 6.5 with sodium hydroxide. Allow to stand for about 2 minutes. Then drain the hydrogen peroxide solution and develop the graphic image by flushing with water for about 30 seconds. Then dry the developed graphic image and proceed with luminescent screen processing.

I claim:

1. A method for producing a luminescent screen structure of a cathode ray tube comprising:

- (a) coating a supporting surface with a film of a polymeric material whose solubility is altered when it is exposed to light,
- (b) exposing said film to an image in the form of said light until the solubility of the irradiated portions thereof is selectively altered, thereby producing in said film regions with greater solubility and regions with lesser solubility,
- (c) removing those regions of said film with greater solubility whereby to bare the areas of the supporting surface underlying said regions of greater solubility, while retaining those regions of said film with lesser solubility,
- (d) overcoating said supporting surface and said retained film regions with a composition which is adherent to said supporting surface, said composition comprising substantially black pigment particles,
- (e) removing at least a portion of said retained film regions and the overcoating composition thereon, while retaining the overcoating composition adhering to said supporting surface, either (i) by baking to volatilize said retained film regions and flushing away the overlying overcoating or (ii) by applying a solu-

tion of a substance that dissolves or degrades said retained film regions into soluble or partially soluble fragments and flushing away the overlying overcoating,

- (f) and then depositing phosphor material on areas of the supporting surface previously occupied by said removed portion of said retained film regions.
2. The method defined in claim 1 wherein said overcoating composition is comprised of solid particles and a binder therefor, said binder being adherent to said supporting surface.
3. The method defined in claim 1 wherein said overcoating composition consists essentially of solid particles which are adherent per se to said supporting surface.
4. The method defined in claim 1, wherein both the coating composition and the overcoating composition are waterbased, and the removal of film regions in step (c) is carried out by the flushing with water.
5. The method defined in claim 1 including, prior to step (d), applying to said retained regions a solution of a chemically-digestive agent therefor, whereby the edges of said retained film regions are dissolved progressively without substantially dissolving the remainder of said retained film regions.
6. A method for producing a luminescent screen structure of a cathode ray tube comprising:
 - (a) coating a supporting surface with a film of a water-soluble polymeric composition whose solubility in water is lowered when it is exposed to light,
 - (b) exposing said film to an image in the form of said light until the solubility of the irradiated regions thereof is selectively lowered, thereby producing in said film regions with greater solubility and regions with lesser solubility,
 - (c) flushing said exposed film with water to remove those regions of said film with greater solubility whereby to bare the areas of the supporting surface underlying said regions of greater solubility, while retaining those regions of said film with lesser solubility,
 - (d) overcoating said supporting surface and said retained film regions with a composition which is adherent to said supporting surface, and which is comprised of substantially black pigment particles, said overcoating being permeable to a solution of chemically-digestive agent for said retained film regions,
 - (e) applying to said overcoating said solution of chemically digestive agent for said retained film regions whereby said agent penetrates said overcoating and solubilizes at least a portion of the retained film regions thereunder,
 - (f) flushing away said solubilized film regions and the overlying overcoating composition, while retaining the overcoating composition adhered to said supporting surface,
 - (g) and then depositing phosphor material on areas of the supporting surface previously occupied by said removed portion of said retained film regions.
7. A method as defined in claim 6, wherein step (e) includes applying to said overcoating an aqueous solution of an oxidizing agent whereby said film regions thereunder swell and softens, and step (f) includes flushing away with water the softened film regions and the overcoating overlying said softened film regions.
8. A method as defined in claim 6, wherein, in step (a), said coating composition consists essentially of a dichromated polyvinyl alcohol; step (e) includes applying to said overcoating an aqueous hydrogen peroxide solution whereby said film thereunder swells and softens; and step (f) includes flushing away the softened overcoating with water.
9. The method defined in claim 6 including, prior to step (d), applying to said retained film regions a solution of chemically-digestive agent to dissolve selectively only marginal portions of the retained film regions.
10. A method for producing a luminescent screen structure upon the inner surface of the glass faceplate of a color

11

television picture tube of the type having an aperture mask therein, said method comprising:

- (a) coating upon said surface a film of dichromated polyvinyl alcohol,
- (b) exposing said film to a light image produced by light projected through said aperture mask until the solubility of the irradiated portions of said film is selectively lowered, thereby producing in said film regions of greater solubility and regions of lesser solubility,
- (c) rinsing said surface with water to remove said regions of greater solubility down to said surface while retaining those regions of lesser solubility,
- (d) overcoating said surface and said retained regions of lesser solubility with a composition consisting essentially of substantially black pigment particles of colloidal size in a liquid medium therefor, said overcoating composition being permeable to an aqueous solution of an oxidizing agent,
- (e) drying said overcoating until said overcoating forms a bond to said surface,
- (f) applying to said dried overcoating said aqueous solution of an oxidizing agent, whereby at least a portion of said retained regions thereunder swells and softens,
- (g) flushing away the softened material and the overlying overcoating,

12

(h) and then depositing phosphor material on areas of the supporting surface previously occupied by said removed portion of said retained film regions.

11. The method defined in claim 10 wherein said pigment particles are graphite particles.

12. The method defined in claim 10 including, prior to step (d), applying to said retained film regions an aqueous solution containing at least one of hydrogen peroxide, an alkali perchlorate, an alkali hypochlorite and an alkali perborate, to dissolve selectively only the marginal portions of said retained film regions.

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U.S. Cl. X.R.

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