May 12, 1970 W. H. MANKO ET AL 3,511,658

PHOTOGRAPHIC REPRODUCTION MATERIALS

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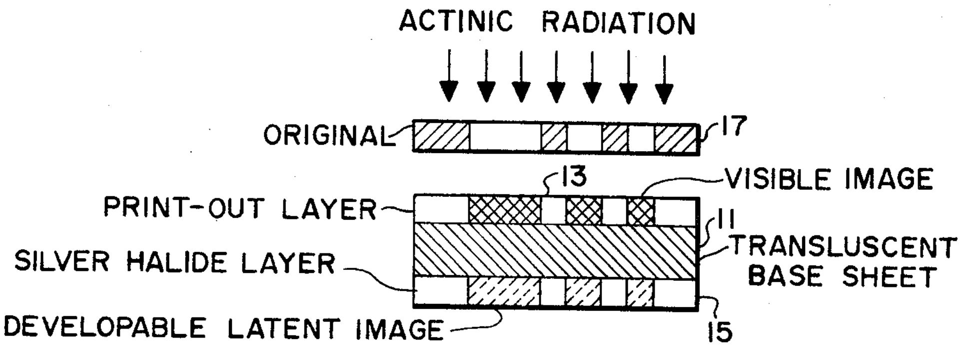

FIG. 1

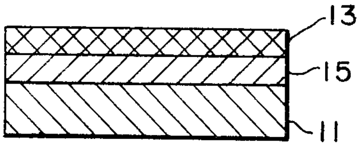

FIG.2

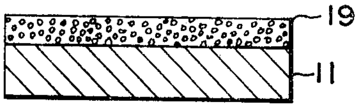

FIG.3

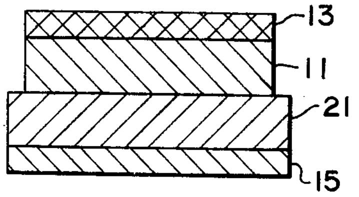

FIG. 4

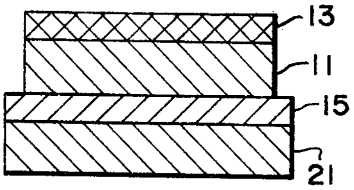

FIG. 5

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PHOTOGRAPHIC REPRODUCTION MATERIALS

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U.S. Cl. 96—68 2 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to photographic reproduction materials which may be used in contact or projection image printing from master transparencies, or may be employed to record graphic intelligence. The materials of the present invention generally comprise composite layers of a direct print-out photographic material and a latent image producing photographic material, whereby photo exposure of the invention material will produce an immediately visible image simultaneously with a latent image which may be later developed to form a visible, high-density image of archival permanence. The print-out image may be employed for immediate interim evaluation of photographic intelligence or may be used as a guide to aid in the registration of additional photographic exposures in processes for preparing composite photographic images.

Composite materials according to the present invention have been found particularly useful when comprising print-out image forming compositions of halogen free-radical dye-forming systems or diazo sulfonate print-out systems, and latent image forming compositions including silver halide components.

BACKGROUND

In the photo reproduction field there is a continuing requirement for systems providing archival permanence in high-contrast images. Materials comprising silver halide photo-sensitive compositions have long been recognized as a means for providing such permanence. Such systems, however, function generally through the physical development of wholly latent images produced by direct contact or projection exposure of graphic originals. Representative systems, such as direct positive and diffusion transfer reproduction processes provide required permanence, but their use is restricted to applications where direct, one-sheet copies of the graphic original will suffice. Due to the latent feature of the copy image before development, silver halide processes are not wholly satisfactory where a requirement for pre-development image proofing or re-touching is required.

Due to the continually increasing rate of developments in the various fields of engineering, the volume of graphic representations of systems, devices and the like, as embodied in particular in engineering drawings, for example, is fast becoming overwhelming. Systems of automated drawing are being developed and are receiving greater attention as a means of employing the great wealth of engineering drawings presently available and to eliminate much of the time-consuming manual drafting procedures heretofore necessary. Such systems employ miniaturized transparencies of basic graphic representations of the particular art involved and through the process of photo-drafting—that is, projection of a series of standard assembly and sub-assembly images in desired registry upon photosensitive sheets—composite engineering drawings are prepared in a small portion of the time previously required of tedious manual drafting techniques.

Some such photo-drafting processes have found increasing acceptance in the engineering fields; however, since commonly available silver halide reproduction sheets are limited by the aforementioned latent image characteristics, the useful photo-drafting processes and techniques have been relatively limited in overall acceptance due to the requirement for physical development of the silver image prior to evaluation of the copied sub-assemblies. Composite general drawing images, therefore, can be prepared according to these previously available systems only through time-consuming exposure and development of various sub-assembly images with final manual registry and preparation of selective negative or projection masters prior to overall exposure and preparation of the whole composite photo-draft engineering drawing.

DESCRIPTION

Now according to the present invention there is provided photographic reproduction material which is capable of furnishing an immediately visible image under exposure to contact or projected light images and which will simultaneously provide a corresponding physically developable latent image capable of producing images or archival permanence. The reproduction materials of the present invention provides, therefore, a means for preparing composite photo-draft engineering drawings and the like through a sequence of exposures of a single sheet to various selected sub-assembly master drawings in readily controllable and discernible registry during reproduction exposure steps and which further provides a means for obtaining in a single development step a complete composite image of good density and contrast, and of archival permanence.

The photo reproduction materials of the present invention generally comprise a base sheet such as paper, plastic film or the like bearing as a coating thereon a first layer of photosensitive, physically developable silver halide composition; and a second layer, coextensive with the silver halide layer, of a composition capable of producing an immediate print-out image upon exposure to actinic radiation. Both the silver halide layer and the print-out composition layer are photographically responsive to incident radiation of substantially the same wave length and are thus photographically responsive to a single exposure of the present photo reproduction material. Exposure of the present material to an image of incident radiation thus provides an immediately visible image in the print-out composition layer and simultaneously forms an identical latent image in the silver halide layer. Additional patterns of actinic radiation may be readily applied to the photo reproduction material in registry with the print-out image or images previously formed and will result in the formation of identically registered latent images in the silver halide layer.

Upon such exposure the material may be subjected to a complete, overall development of the latent image or may, prior to development, be treated so as to remove, as desired, certain portions of the latent image as defined by the visible print-out image. During the development process the print-out image may be entirely removed, if desired, so as to provide a single silver halide image on the sheet.

The construction of a sheet according to the present invention may be more readily understood with reference to the accompanying drawing wherein:

FIG. 1 shows a cross section of one embodiment of the photo reproduction material wherein the print-out composition layer and silver halide layer are disposed on opposite sides of the carrier sheet. The typical location of an original master during photographic exposure is also shown.

FIG. 2 represents the cross section of another embodiment of the invention wherein the print-out and silver halide layers are disposed on the same side of the carrier sheet;

FIG. 3 shows the cross section of another embodiment of the invention wherein the silver halide composition is intimately disposed in the layer of print-out composition on the support layer;

FIG. 4 shows the cross section of another embodiment of the invention wherein the print-out layer and silver halide layer are disposed on separate carrier sheets and the sheets are located in back-to-back relationship;

FIG. 5 shows the cross section of another embodiment of the invention wherein separate sheets bearing the print-out layer and silver halide layer are positioned in back-to-face relationship.

As will be observed with reference to FIG. 1, a radiation transparent or translucent base sheet **11** is coated on one face with a sufficient amount of a photosensitive print-out layer to provide a readily discernible or visible image upon exposure to actinic radiation. The reverse side of the base sheet is coated with a layer of silver halide composition **15**, such composition being photolytically responsive to actinic radiation of a wave length substantially identical to that which will provide a print-out image in the composition of layer **13**. Such positioning of the respective photosensitive layers on opposite sides of the base sheet is preferred, since both layers are readily accessible to treatment during or after exposure, or prior to physical development, for example, the silver halide layer may be altered by removal of latent image areas during the various exposing steps in the sequential projection of master images to provide a composite photodraft drawing. A further advantage of the interposition between the photosensitive layers of the support is found in that the support itself may be used to provide a filtering medium or radiation absorptive medium which will compensate for inherent differences in photoresponsivity of the print-out and silver halide compositions. Exposure of the print-out image composition may thus be sufficiently reduced in passing through the base sheet to prevent overexposure of the silver halide layer which might otherwise occur due to a greater sensitivity of the silver halide composition. Additional radiation absorbers may be included in the base sheet or in an intermediate layer thereon if desired.

The interposition of the base sheet between the two photosensitive layers is not necessary, however, as will be noted with reference to FIG. 2 wherein the print-out layer **13** and the silver halide layer **15** may be juxtaposed. In such constructions, the compositions of the respective layers are selected so as to provide more closely approximate sensitivities. An additional variant in the construction of photoreproduction material according to the present invention is represented in FIG. 3 and comprises, as a signle photosensitive layer **19**, a dispersion of a photosensitive silver halide composition with a photosensitive print-out composition. It will be apparent that in either of the embodiments represented by FIGS. 2 and 3, the base sheet **11** need not be transparent or translucent to the actinic radiation and further that the separate accessibility of the latent image layer is not provided. In general usage, as with the direct photocomposition of engineering drawings from various sub-assembly masters, such accessibility is not necessary and may be readily dispensed with.

For use in photocomposition processes, as referred to above, it is particularly desirable that the print-out and latent image forming photographic compositions be photolytically responsive, at most, to only a small portion of the visible light wave band. Such a selection of photolytic response provides a useful range of visible light in which manual manipulation of the reproduction materials and exposure devices may be accomplished without danger of overexposing or fogging the desired photographic images on the reproduction material while at the same time providing an effective range of exposure wavelengths for the material. It has been found particularly desirable to employ photographic compositions responsive to wavelength ranges of from about 3,000 to 5,000 angstroms and which are non-responsive to longer wavelengths, such, for example, as obtained in yellow safe-light conditions. The print-out image compositions are therefore selected so as to provide images of a distinct color which is clearly visible under such conditions; for example, blue images where yellow safe-light environment is employed.

The invention is described in greater detail in the following examples.

In a number of the examples where separate print-out layers and silver halide latent image producing layers are employed, a commercial ultraviolet sensitive silver halide coated paper was used as the base sheet for the material to be prepared according to the present invention. Such presensitized sheet material is readily available in the form of Peerless UV 55 gram and Peerless UV 80 gram papers, and Eastman-Kodak Wash-Off Drafting Film, a UV sensitized 4 mil polyester film base.

EXAMPLE 1

The back side of a sheet of Peerless UV 55 gram contact paper was coated to a wet thickness of 1.5 mil with a composition consisting of:

Styrylacrylonitrile—0.60 gm.
Acetone—8.7 ml.
Denatured ethanol—1.3 ml.
Diphenylamine—0.75 gm.
Carbon tetrabromide—1.10 gm.

and dried in circulating air. The sheet thus prepared was exposed at the print-out composition side under a contact negative original and Pyrex glass sheet to the light of a General Electric 275 watt sunlamp from a distance of about 10 inches for a period of about 25 seconds. A positive print-out image resulted which was clearly visible through the sheet under yellow safe-light conditions. The whole sheet was then subjected to normal silver halide photographic development and fixing, and there resulted a clear, high density image corresponding exactly to the previously obtained print-out image. The developed sheet was heated for about three minutes at 100° C. to desensitize the print-out image composition. Both the silver halide and print-out image thus remained on the base sheet. Desensitization of the print-out composition was obtained also by a washing with organic solvent to physically remove the print-out composition layer.

EXAMPLE 2

The unsensitized surface of a sheet of Peerless UV 55 gram photographic paper was coated to a wet thickness of 1.5 mil with the following composition and dried in warm air:

Cellulose acetate—0.5 gm.
Acetone—10.0 ml.
Carbon tetrabromide—1.2 gm.
Diphenylamine—1.0 gm.

The side of the sheet thus coated was exposed under a negative transparency and a Pyrex glass sheet to a 275 watt sunlamp at a distance of about 12″. A clear blue print-out image resulted after about 30 seconds exposure and subsequent silver halide development and fixing produced a clear, high density silver image which was visible with the print-out image. Heating at about 100° C. for a period of three minutes fixed the print-out layer against subsequent fogging.

EXAMPLE 3

The diphenyl amine of Example 2 was substituted by 0.71 g. of leuco malchite green and 0.10 g. of triethanol amine. The resulting composition was coated to a wet thickness of 1.5 ml. on the unsensitized surface of a sheet of Peerless UV 55 gm. Photographic Paper and dried. Exposure to a 275 w. sunlamp through a negative transparency and a Pyrex glass plate resulted in a legible blue-green image in about 70 seconds. Conventional silver halide development and fixing of the sheet provided a usable high-density silver image. The print-out image layer was desensitized against subsequent fogging by washing in a 1:1:3 mixture of acetone:toluene:heptane.

EXAMPLE 4

The commercially-available ultraviolet-sensitive silver halide paper described in the foregoing examples was coated to a wet thickness of 1.5 ml. with the following composition and dried:

5% polystyrene in benzene—8.0 ml.
Leuco crystal violet—0.64 g.
Hexachloroethane—0.8 g.
Triethanol amine—0.13 g.
Acetone—2.0 ml.

Exposure of the resulting sheet through a negative transparency to the light of a 275 w. sunlamp yielded a clear, legible print-out image and subsequent development and fixing of the latent silver halide image according to conventional procedures resulted in a clear, high-density, well-defined silver image. The print-out image was fixed by washing with the solvent mixture as described in Example 3.

EXAMPLE 5

A silver halide sensitizing composition was prepared as follows, coated to a wet thickness of 3 ml. on a polystyrene impregnated rag paper and dried and aged for several days.

The following solutions were prepared with distilled water:

(A) silver nitrate 20 g.—water to make 100 ml. solution;
(B) water 85 ml.—potassium chloride 10 g.—nickel chloride 2.5 g.—cupric chloride 5.5 g.
(C) 10% gelatin solution in water.

About one-third of Solution (B) was added to the gelatin solution and the mixture was heated to 50° C. One-third of the (A) solution was then added and the mixture held at 50° C. with continuous stirring. The remaining portions of Solutions (A) and (B) were alternately added in one-third portions and the entire mixture held at 50° C. for about ten minutes and then cooled rapidly to 30° C. Ten ml. of 10% aqueous solution of saponin, 12 ml. of diethylene glycol, 8 ml. of 5% chrome alum solution and 3 ml. of 40% formaldehyde were added to the silver chloride composition with thorough agitation.

The silver chloride-sensitized sheet thus prepared was coated on the reverse side with a 1.5 mil wet thickness of the following composition and air dried:

Cellulose acetate—0.5 g.
Acetone—10.0 ml.
Carbon tetrabromide—1.2 g.
Diphenyl amine—1.0 g.

Exposure of the diphenyl amine coated side of the sheet to the above-mentioned sunlamp source for about 15 seconds produced a readable, blue print-out image. Conventional developing and fixing resulted in a clear, high-density silver image on the reverse side of the sheet. Heating the sheet at 100° C. for about three minutes fixed the print-out image against subsequent fogging.

EXAMPLE 6

The back side of the sheet of Peerless UV 55 g. Paper

was coated to a wet thickness of 1.5 ml. with the following formulation and air dried:

Styroacrylonitrile—0.1 g.
Actone—8.5 ml.
Diphenylamine—0.75 g.
Trichloromethylphenylsulfone—0.49 g.
Ethanol—1.5 ml.

A 30× enlarging projector utilizing a 500 w. UV source was used to project the image of a negative transparent master onto the thus coated surface of the sheet. Exposure was continued for about 3 minutes; the light falling upon the sensitized surface of the sheet being of an energy level of about 30 microwatts per square centimeter in the wave length range of 3,000–5,000 angstroms. Very little energy below about 3,200 AU survived passage through the optical system. A good, readable print-out image was obtained. It was wholly visible under yellow safelight conditions. The negative transparency was then replaced by a second transparency under safelight conditions and by means of the interposition of an optical filter which removed bands of the source light below about 5,000 AU, a second image was projected on the sensitized sheet material and brought into proper registry with the print-out image previously obtained. After the establishment of registry, the filter was removed and the surface of the sheet was exposed to the actinic range of 3,000–to-5,000 AU emitted by the optical system. After about a three-minute exposure a readily-visible composite print-out image was available. Conventional silver halide development and fixing of the whole sheet produced a single composite, clear, dense silver image with no apparent fogging or background development. The diphenyl amine print-out composition was desensitized against subsequent fogging by immersing the sheet for two minutes in an aqueous solution of 5% sodium sulfite and 4% glycerin and drying the sheet for about three minutes in a forced draft oven at about 140° C.

EXAMPLE 7

The silver halide sensitized side of a sheet of Peerless UV 80 gm. paper was coated to a thickness of 1.5 ml. with the following print-out composition and dried:

Cellulose acetate—0.5 g.
Acetone—10 ml.
Carbon tetrabromide—1.2 g.
Leuco malachite green—0.71 g.
Triphenyl stibine—0.2 g.

The coated surface of the resulting sheet was exposed from a distance of about 12 in. through a Pyrex plate and an original transparency to the light of a 275 w. sunlamp for about 15 seconds. A clear print-out image was readily visible under yellow safelight conditions. Areas of the print-out image layer were removed with acetone and upon conventional silver halide development there was produced a high-density image corresponding to the original print-out image. The silver halide development did not occur in those areas located beneath the remaining print-out layer. Subsequent removal of the print-out layer and conventional silver halide fixing resulted in a clear background in these areas. This procedure may be employed as a means of altering the image of exposed sheets.

EXAMPLE 8

A sheet of polyethylene terephthalate bearing a subbing layer of cellulose acetate butyrate was coated with the following composition and air dried:

Methyl isobutyl ketone—10.8 ml.
Isopropyl acetate—6.5 ml.
Diphenylamine—3.2 g.
Carbon tetrabromide—3.8 g.

The resulting sheet was placed in back-to-back combination with a sheet of Peerless UV 55 gram paper as generally shown in FIG. 4. Exposure of the composite structure through a Pyrex plate and original transparency to the light of a 275 w. sunlamp for about 35 seconds at a distance of about 15 inches resulted in a blue printout image in the plastic film layer which was clearly readable in yellow light. Separation of the sheets and conventional silver halide development of the photographic paper resulted in a clear, high-density silver image. Permanence of the silver image was obtained by means of conventional photographic fixing.

EXAMPLE 9

The print-out composition of Example 8 coated on 2.5 mil tracing paper was assembled with the silver halide sheet as in FIG. 5. Exposure of the print-out layer to the 275 w. sunlamp as in Example 8 resulted in a readable blue image in about ten seconds. Separation of the sheets and normal photographic development of the silver halide coated paper provided a permanent silver image of good density and excellent detail.

EXAMPLE 10

The following compositions were prepared and were mixed together in volume portions of 20:8:10 and coated to a 3 mil wet thickness on 55 gram baryta coated base paper.

Composition A: The silver chloride contact speed emulsion described in Example 5.

Composition B:

Methylene chloride—7 ml.
Methanol—10 ml.
Diphenylamine—1 g.
Tribromo methylphenyl sulfone—1 g.
Thioflavine T (CI No. 49005)—5 g.

Composition C:

Gelatin—10 g.
Water—100 g.
Diphenylamine—1 g.
Carbon tetrabromide—1 g.

The resulting material was exposed about three days after coating to a projected light image of an energy density of about 30 microwatts per sq. centimeter from an enlarging projection system as described in Example 6. An exposure of about one minute produced a blue image readable under yellow safelight conditions. After conventional silver halide development the print-out image was entirely obscured by an identically disposed high density silver image. The image thus obtained was permanently fixed by conventional fixing and washing.

Numerous print-out compositions are known which are sensitive to ultraviolet radiation, many being described in such U.S. patents as 3,042,515; 3,042,516; 3,095,303; and 3,100,703. Color-forming print-out compositions of this general type may be employed in the reproduction materials of the present invention. Useful activator materials for such color-forming compositions include, in addition to materials set forth in the foregoing example, pentabromoethane, hexabromoethane, o-bromo biphenyl, bromo acetic acid, 2,4 dichlorophenoxy acetic acid, p-nitrobenzene sulfonyl chloride, bis-(tribromomethyl)sulfone, tribromoquinaldine, tribromoacetophenone. Additional color formers which have been found useful in preparing print-out image compositions for use in yellow safelight environment include Michler's base and leuco opal blue.

In addition to color-forming printout compositions based upon so-called free radical activity, such as are described in the foregoing examples, certain diazo sulfonate compositions have been found to be equally effective in preparing reproduction materials according to the present invention.

EXAMPLE 11

The uncoated side of a sheet of Peerless UV 55 gram paper was coated to a 1.5 mil wet thickness with a 10% solution of polystyrene in benzene and was air dried. An overcoating of about 1.5 mil wet thickness of a 5% solution of cellulose acetate in acetone was then applied and air dried. A coating of about 1 mil wet of the following composition was then applied to this composite barrier layer and dried.

Distilled water—83 ml.
Acrylic acid amide—50 gm.
Thiourea—0.5 gm.
1,3,7 trimethyl xanthine—3.0 gm.
4'diazo-2'5'diethoxy benzanilide, zinc chloride salt— 2.0 gm.

To the above solution 0.8 gram of sodium sulphite dissolved in 25 ml. of water was added. After thorough mixing 5.0 ml. of triethanolamine was added to the solution to bring the pH to between about 9 and 10. The coating composition was completed by adding 0.67 gram of 2,3 dihydroxy naphthalene.

The dry sheet thus prepared was exposed through a negative original for about 12 seconds from a distance of 1 ft. with a 275 w. sunlamp and there resulted a blue printout image which was readable through the sheet under yellow safelight. Conventional silver halide development provided a corresponding dense, fully detailed, silver image which was fixed in the normal manner. The printout image was readily removable with organic solvents such as acetone or toluene.

Similarly useful barrier layer compositions included 10% polyvinyl chloride in tetrahydrofurane, 10% styryl acrylonitrile in acetone, and 7% polyvinyl alcohol in water, in hydrophobic/hydrophilic combinations.

EXAMPLE 12

Reproduction material was prepared by applying the coatings of Example 11 in the same manner to the silver halide coated face of Peerless UV 55 gm. paper. Subsequent to composite image-forming exposure as described in Example 6, portions of the diazo printout image layer were selectively removed with organic solvent and the sheet was subjected to overall normal silver halide development. A clear, dense silver image corresponding to the printout image was obtained in the areas where the printout image layer had been removed. Normal photographic fixing baths removed the remaining diazo printout image layer and completely fixed the silver image. A clean background was thus provided in areas of the sheet from which the diazo layer was not removed before silver development and which were not originally exposed. By manual drafting, parts variations were inserted into the partial layout image and a new master was thus prepared from which complete layout reproductions were made in the normal manner.

What is claimed is:

1. Photographic reproduction material comprising:

(A) a support;

(B) a photosensitive, developable-image silver halide composition; and

(C) a photosensitive printout image composition which undergoes a visible color change upon exposure to actinic radiation;

said compositions having a common photolytic spectral sensitivity range and being intimately admixed and disposed substantially coextensive with respect to said support.

2. Photographic reproduction material comprising:

(A) a support

- (B) a photosensitive, developable-image silver halide composition; and
- (C) a photosensitive printout image composition comprising, in an alkaline condition:
  - (a) the sulfonate of a photosensitive diazonium compound;
  - (b) an acrylic acid amide; and
  - (c) an azo dye coupler capable of forming a distinctly colored dye with said diazonium compound;

said compositions having a common photolytic spectral sensitivity range and being disposed substantially coextensively with respect to said support.

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DAVID KLEIN, Primary Exaiminer

U.S. Cl. X.R.

96—27, 41, 67

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,511,658 Dated 12 May 1970

Inventor(s) William Manko and Leonard May

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

At Column 7, line 37, "5g." should read — 5mg.--

SIGNED AND
SEALED
SEP 15 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents