United States Patent Office 3,547,634 Patented Dec. 15, 1970

3,547,634

LIGHT SENSITIVE COMPOSITION CONTAINING A HETEROCYCLIC PHOTOACTIVATOR HAVING AN —N⁺=C— GROUP IN THE HETEROCYCLIC RING ALKYL THEREOF AND THE PHOTOGRAPHIC USE THEREOF

Haruo Hori and Shoichiro Hoshino, Tokyo, and Hiroshi Tokura, Tsuru-shi, Japan, assignors to Keuffel & Esser Company, Hoboken, N.J., a corporation of New Jersey

No Drawing. Filed Oct. 26, 1966, Ser. No. 589,495
Claims priority, application Japan, Nov. 2, 1965, 40/67,025
Int. Cl. G03c 5/24
U.S. Cl. 96—48 6 Claims

This invention relates to light-sensitive reproduction material comprising a photo-activatable component which becomes reactive by action of light and a color-formable component which develops color by reaction with said photo-activatable component in a reactive state. An object of the invention is to provide reproduction material which is inexpensive and easily handled and which gives a clear and stable color image high in resolving power.

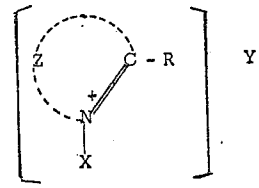
As the so-called printing-out materials which develop images by action of light, there have conventionally been known silver printing-out photographic papers (P.O.P. paper) using a light-sensitive silver salt as the the main component; blue-print papers using a light sensitive iron salt as the main component; compositions using organohalogen-containing compounds yielding free halogen groups by action of light, such as disclosed in U.S. Pat. Nos. 3,042,515, 3,042,519; and compositions containing as a light-sensitive component a leucocyanide of a triphenylmethane dye, such as disclosed in U.S. Pat. No. 2,676,887.

Such conventionally known materials, however, have more or less suffered, respectively, from such drawbacks that they are relatively expensive, the resulting images are unstable and they encounter various difficulties in handling. For example, the printing-out photographic papers are excellent in tone quality of images, but they are not only expensive but are low in sensitivity and the stability of the resulting images is not satisfactory. In the case of the blue-print papers, the resulting images are excellent in stability, but they suffer from such drawbacks as being poor in tone quality, low in sensitivity and inferior in resolving power. Further, in the case of the compositions using organohalogen-containing compounds, there have been such difficulties that the photo-activatable components employed are extremely poisonous and are volatile, and therefore close attention is required in handling light-sensitive papers using said compositions. The printing-out compositions of the present invention are less in such difficulties as compared with the conventionally known printing-out materials and are markedly excellent. That is, the printing-out compositions of the present invention contain no poisonous component and are easily handled, and the resulting printed-out images are not only satisfactory in tone quality and show a prominent resolving power, but also are excellent in stability.

The light-sensitive printing-out composition of the present invention comprises a photo-activatable component selected from the group consisting of compounds represented by the general formula shown below, and a color-formable component which develops color by reaction with the photo-activatable component brought into a reactive state. A printing-out material obained by use of the composition of the present invention directly develops color on exposure to active radiation such as ultraviolet or visible light. Therefore, when the material is placed on a photographic negative or an original and printing is effected by use of such light, it is possible

to obtain a clear print-out image, which can then be made into a stable image by a subsequent fixing operation. Both of the above-noted components employed in the composition of the present invention are non-toxic and stable substances and are easily obtainable, and therefore a printing-out material obtained therefrom is not only safe in handling, but also excellent in storability and can be provided at a low cost.

The structure and effects of the present invention will be explained in full detail below. The first components employed in the present invention are photo-activatable compounds capable of being brought into a reactive state by action of light and are represented by the general formula



wherein R is a C_1–C_3 alkyl group or aralkyl group; X is a C_1–C_4 alkyl group, aralkyl group or acid group; Y is an anion group, provided, however, that X may be such a group that an anion is added to the terminal of a lower alkylene to form, together with nitrogen, an intramolecular salt, Y being unnecessary in such a case; and Z is an atomic group necessary to form a simple or complex heterocyclic ring having or not having a 5-membered or 6-membered substituent together with C and N.

Examples of such photo-activatible components are 2-methyl-benzothiazole-methyl iodide, 2 - methylbenzothiazole-ethyl iodide, 2-methylbenzothiazole - n - butyl iodide, 2 - methylbenzothiazole-ethyl p-toluenesulfonate, 2-methylbenzothiazole-benzyl bromide, 2 - methylbenzothiazole-ethyl fluoroborate, 2-methylbenzothiazole-propionic bromide, 2 - methyl-5 - chlorobenzothiazole-ethyl p-toluene-sulfonate, 2 - methyl - 6 - ethylbenzothiazole-methyl iodide, 2,6 - dimethyl-benzothiazole-ethyl fluoroborate, 2 - methyl - 6 - ethoxybenzothiazole-propyl bromide, 2-methyl-5,6 - diethoxybenzothiazole-propyl bromide, 2,5,6-trimethylbenzothiazole-ethyl p-toluene- sulfonate, 2-methylnaphthothiazole-ethyl fluoroborate, 2,4,5-trimethylthiazole-ethyl fluoroborate, 2 - methyl-4,5 - diphenylthiazole-methyl iodide, 2-methylbenzoselenazole-ethyl bromide, 2,5 - dimethylbenzoselenazole - n - butyl iodide, 2 - methyl-5-ethoxybenzoselenazole-ethyl p-toluenesulfonate, 2 - methylnaphthoselenazole-ethyl p-toluenesulfonate, 2 - methyl - 5 - phenylbenzoxazole - ethyl iodide, 2 - methyl - 5 - phenylbenzoxazole-ethyl bromide, N-ethyl - 2 - methyl - 5,6 - dichlorobenzimidazole-methyl iodide, 2-methylpyridine-ethyl iodide, 2-methylpyridine-methyl iodide, 2-methylpyridine-methyl p-toluenesulfonate, 2 - methylquinoline-methyl iodide, 2 - methylquinoline-ethyl iodide, 2 - ethylbenzothiazole-ethyl iodide, 2-benzylbenzothiazole-methyl iodide, 2 - phenethylbenzothiazole-ethyl iodide, 2 - methylbenzothiazole - butyrosultone, 2,5,6 - trimethylbenzothiazole-n-butyrolactone, 2 - methylbenzothiazole-ethyl sultone, 2-methyl-5-ethoxybenzoselenazole-n-butyrosultone. In addition thereto, there are many effective compounds conforming to the general formula, and photo-activatable components usable in the present invention are not limited to the above examples.

The heterocyclic compounds employed as the first components in the present invention do not develop color by themselves by action of light, but are brought into an active state strong in reactivity by action of light and react with color-forming components to develop color,

thereby forming coloring matters by which images are formed.

The second components employed in the present invention in combination with said photo-activatable components, the first components, are color-formable components. The color-formable components do not develop color by themselves by action of light, as in the case of the photo-activatable components, but develop color by reaction with the photo-activatable components, which have been brought into a reactive state by action of light, to form coloring matters. The color-formable components having such properties as mentioned include chemical substances of a markedly wide scope, and cannot be exemplified as substances having structures of a specific scope. In short, color-formable components usable in the present invention include all such substances as develop color when exposed to light in combination with the above noted photo-activatable components.

Appropriateness of a compound as a color-formable component may be determined by dissolving said compound together in about equal proportions with a selected photo-activatable component (e.g., 2-methylbenzothiazole-methyl iodide), coating the solution on a paper and then, after drying, exposing the paper to light. If color is developed, the tested compound can be considered suitable as a color-formable component. When classified according to groups or bonds contained therein, compounds which have been clarified to be effective by this test method are as exemplified below. It is, however, needless to say that other compounds than those exemplified below are also utilizable so far as they have been found to have color developing properties according to said test.

Useful materials include (nitrile groups): p-nitrobenzonitrile, benzoyl acetonitrile, p-nitrobenzyl cyanide and p-aminobenzoyl acetonitrile; (carbonyl bonds): benzylacetone, p,p'-tetramethylaminobenzophenone, benzophenone, phenylbenzylketone, 3 - pyridyl-4-quinolylketone, B-naphthoquinone, benzoquinone, anthraquinone and phenanthraquinone; (aldehyde groups): o-phthalaldehyde, o-phthalaldehydic acid, 2,4 - dihydroxybenzaldehyde, p-dimethylaminobenzaldehyde, terephthalaldehydic acid, 3-hydroxy - 4 - methoxybenzaldehyde, B-naphthoaldehyde, -naphthoaldehyde, 2,4 - dichlorobenzaldehyde, p-nitrobenzaldehyde, salicylaldehyde, p-hydroxybenzaldehyde, m-nitrobenzaldehyde, o-nitrobenzaldehyde and 5-bromosalicylaldehyde; (nitroso groups): N-nitrosodiphenylamine, phenyl - 2 - naphthylnitrosamine, 1-nitroso-2 - naphthol-3 and sodium 6-disulfonate; (amino groups and nitrogen-containing compounds): B-naphthylamine, acetanilide, diphenylguanidine, phenazine, hexamethylenetetramine, diphenylamine, vinylcarbazole, indole, phenyldiethanolamine, tetramethyldiamino - diphenylmethane, N,N'-diphenyl-p-phenylenediamine, vinylurea, salicylidene-p-toluidine, o-nitrobenzal - B-naphthylamine, salicylidene-o-chloroaniline, salicylidene aniline, o-nitrobenzalisonicotinic acid hydrazide, salicylidene-B-naphthylamine, p-anisalphenyl hydrazide, salicylidene-o-anisidine, benzalphenyl hydrazide, o - nitrobenzal - p'-anisidine, o-nitrobenzal-p-nitroaniline, salicylidene-p'-bromoaniline and n-bromo-salicylidene benzylideneamine. As mentioned before, however, not only the compounds cited above but also those developing color in the aforesaid test are all usable as the color-developing components in the present invention.

The light-sensitive, printing-out composition of the present invention comprises the above-mentioned two components and, depending on the combination of photo-activatable component and color-formable component, the sensitivity of the resulting composition and the color tone of the coloring matter variously change. For example, the developed color tones and sensitivities of printing-out materials obtained from compositions prepared by using o-phthalaldehydic acid (OPA) and diphenylamine (DPA) as color-formable components and combining said components with various photo-activatable components are as

shown in the table below, in which the sensitivities of the materials are represented by the number of stages of wedges printed-out when the materials have been subjected to a given light source through optical wedges of 0.20 in stage difference.

Photo-activatable component	OPA	DPA
2-methylbenzothiazole-methyl-p-toluenesulfonate.	Purple, 8 stages.	Light brown, 5 stages.
2-methyl-5-chlorobenzothiazole-ethyl p-toluenesulfonate.	Brown, 12 stages.	Light brown, 6 stages.
2-methylnaphthothiazole-ethyl p-toluene sulfonate.	Green, 12 stages.	Blue, 8 stages.
2,5-dimethylbenzothiazole-methyl fluoroborate.	Purple, 13 stages.	Reddish purple, 15 stages.
2-methylbenzothiazole propionic acid bromide.	Bluish purple, 13 stages.	Reddish purple, 13 stages.
2-methyl-6-ethoxybenzothiazole-propyl bromide.	Blue, 15 stages.	Brown, 9 stages.
2-methylbenzothiazole-ethyl iodide.	Purple, 13 stages.	Blue, 11 stages.
2-methylbenzoselenazole-ethyl iodide.	Blue, 10 stages.	Blue, 8 stages.
2,5-dimethylbenzoselenazole-butyl iodide.	Blue, 14 stages.	Blue, 9 stages.

As mentioned before, the light-sensitive printing-out composition of the present invention comprises two components of the photo-activatable component and the color-formable component, and a printing-out material prepared by use of said composition directly develops color by the action of light, particularly ultraviolet light, to give a clear image high in resolving power. It is to be understood, however, that additional components such as sensitizers and a fixation-improving agent may be incorporated, if necessary, to further improve the characteristics of the resulting printing-out materials. As the sensitizers, there are two types; those which enhance the sensitivity itself of the present light-sensitive, printing-out compositions and those which enhance the sensitivity by broadening the wave length area of a light to which the present compositions are exposed.

As the sensitizers belonging to the former type, organic and inorganic metal salts and ammonium salts are effective. Examples thereof are sodium chloride, calcium, potassium bromide, sodium fluoride, aluminum fluoride, zinc fluoride, barium fluoride, sodium sulfate, zinc lactate, lead stearate, sodium pyroracemate, sodium hypophosphite, ammonium rhodanate and ammonium citrate. In addition thereto, heterocyclic compounds such as benzothiazole, benzoxazole, pyridine and quinoline are also effective. Further, when white pigments such as titanium white, zinc oxide or alumina powder are added, these pigments adsorb the coloring matters formed, whereby the developed color density increases to apparently enhance the sensitivity. Thus, the white pigments show the same effects as those of sensitizers.

As the sensitizers belonging to the latter type, i.e. those which enhance the sensitivity by broadening the wave length area of a light to which the present compositions are exposed, sensitizing coloring matters known in the conventional photography, such as those belonging to cyanine, xanthene and acrydine series, are effective. Examples of these are pinacyanol, pinacryptol yellow, eosine, iodoeosine, Rose Bengal, auramine, Thioflavin-T, Erythrocin-B, Bromothymol Blue, and Acridine Orange. By proper use of these sensitizers, the sensitivities of the present printing-out compositions can be enhanced up to about tenfold, and printing-out materials prepared by use thereof become sensitive not only to ultraviolet ray, but also to visible rays. Therefore, it also becomes possible to obtain images by enlarged printing from photographic negative using an incandescent lamp as a light source.

Other components which are desirably incorporated into the present light-sensitive, printing-out compositions are fixing property-improving agents. Printing-out materials prepared from the present printing-out compositions are fixed, after printing, by subjecting to heat treatment using a hot roll or the like, in general, and become stable thereafter to irradiation of light. In this case, the addi-

tion of weakly reducing substances such as nitrites, sulfites, hydrazines and hydroxylamines makes it possible to improve the fixing property and further the stability of the resulting images.

As is clear from the above explanation, the light-sensitive printing-out composition of the present invention is prepared by using as primary components at least one photo-activatable component and at least one color-formable components and, if desired, incorporating additional components as sensitizer and fixing property-improving agents. A useful novel printing-out material can be obtained by applying such a composition to a suitable support.

The printing-out material is preferably prepared by dissolving or finely dispersing the components in an appropriate solvent or fluid vehicle, and coating the solution or dispersion onto a support, followed by drying.

A printing-out material of improved physical property can generally be obtained by using as a binder a film-forming high molecular weight substance soluble in the coating liquid. Such high molecular weight substances useful as binders include polyvinyl alcohol, carboxymethyl cellulose, hydroxyethyl cellulose and maleic anhydride copolymers, cellulose derivatives such as cellulose acetate, cellulose acetate butyrate and ethyl cellulose; vinyl polymers or copolymers of vinyl chloride, vinylidene chloride, vinyl acetate, acrylate ester and styrene; copolymers of maleic anhydride; and synthetic rubbers such as cyclized rubber, acryl rubber and butadiene copolymers. Useful solvents and vehicles include, in addition to water, alcohols such as methanol, ethanol and propanol; ketones such as acetone and methylethylketone; hydrocarbons such as benzene, toluene, xylene, hexane and ligroin; halogenated hydrocarbons such as methylene chloride and trichloroethylene; and esters such as ethyl acetate and amyl acetate. In addition thereto, tetrahydrofuran, dimethylformamide and cyclohexanone can be used. These may also be used in the form of mixed solvents such as hydrated methanol and acetone-methanol.

Suitable supports, to which are to be applied the present printing-out compositions are papers such as photographic papers, plastics-coated papers and copying papers, in general. However, cellulose acetate films or plastic sheets prepared from polyethylene terephthalate and polycarbonate are also preferable. Further, glass sheets or metal sheets can also be used depending on purposes.

The application of the present light-sensitive printing-out compositions to supports is effected in a dark place according to various coating methods known heretofore. In place of preparing printing-out materials by coating supports with the coating compositions obtained in the above manner, however, the printing-out materials may also be prepared, in specific cases, by forming respective components into fine particles, blending the finely divided particles and rubbing the resulting mixture into the surface of a support using a buff roll or the like, or incorporating the components into a paper material during paper-making step and subjecting the paper to sizing treatment. The compositions for preparing the present light-sensitive, printing-out materials may generally comprise the following:

	Parts by weight
Solvent	1,000
Binder (optional)	5–30
Photo-activatable component	10–100
Color-formable component	10–100
Sensitizer (optional)	0.1–10
Fixing property-improving agent (optional)	5–200

For the exposure of the reproduction materials of the present invention, a commercially available copying machine for diazotype light-sensitive papers which uses a mercury lamp or fluorescent lamp as a light source can be advantageously used. When the exposure is desired to be effected according to reflex printing, there may be used a printing machine for diffusion transfer copying. Further, printing-out materials prepared from the present compositions sensitized with coloring matters are consdierably high in sensitivity, and therefore enlarged prints can also be obtained from photographic negatives using an enlarger or slide projector.

When left untreated, the exposed printing-out materials remain light-sensitive and therefore the images are required to be fixed so as to become stable. This fixation is most simply effected by thermal exposure, in general. The thermal fixation is easily carried out by passing the printing-out materials between hot rolls having a surface temperature of about 100°–180° C. In addition thereto, the material may be inserted between hot plates, or the heating may be effected by use of an electric heater. The fixation can be carried out not only by said heating but also by treatment with solvent, though the latter is more or less troublesome in operation. The solvent treatment is conducted by immersing the printing-out material, after printing, in a solvent which does not dissolve coloring matters formed by exposure, but dissolves the components remaining in unexposed portions. For example, in the case of a printing-out material prepared from a light-sensitive, printing-out composition comprising 2-methylbenzothiazole-methyl p-toluenesulfonate and diethylamine, the resulting images can be solvent-fixed with such a solvent as acetone, methylethylketone or ethyl acetate. The use of a solvent of the alcohol series is not desirable, however, because the coloring matters formed are dissolved out. The solvent fixation does not always require the use of organic solvents, but can also be effected in water or in solutions formed by dissolving suitable salts in water. Images subjected to thermal fixation or solvent fixation in the above manner are stable to light and maintain clear color tones without discoloration even when exposed to direct sunlight for several days.

The following examples illustrate the present invention, but the invention is not limited to the examples, and various applications are possible within the scope of the invention.

EXAMPLE 1

40 g. of 2-methyl-5-ethoxybenzosalenazole-p-toluenesulfonate as a photo-activatable component and 60 g. of o-phthalaldehydic acid were dissolved in 100 ml. of water in a dark room to form a light-sensitive, printing-out composition. The thus obtained composition was coated according to a normal procedure on a common photographic grade base paper of 45 g./m.^{2} in thickness and was dried in a dark place at a temperature of below 60° C. to obtain a printing-out material. On this printing-out material was placed a photographic negative, and the composite was exposed for 5 seconds to a 800 w. high pressure mercury lamp at a distance of 3 cm., whereby the printing-out material immediately developed color to give a deep bluish green clear positive image on a white ground. Since the unexposed portions of the material develop color by action of light when the material is left untreated, the image was fixed by passing the material between hot drums having a surface temperature of 160° C. By this fixing treatment, there was obtained a stable image which was not discolored even when directly exposed to sunlight. The maximum density of the image was 1.40 and the fog portion was 0.02. The image obtained was a positive image which had faithfully reproduced the tone of the original negative.

EXAMPLE 2

50 g. of 2-methylbenzothiazole-methyl iodide as a photoactivatable component and 50 g. of N-nitrosodiphenylamine were dissolved in 1000 ml. of a 1:1 mixed solvent of acetone and methanol to obtain a light-sensitive, printing-out composition. The thus obtained composition was coated, according to a known procedure, on a photographic baryta paper and was dried to prepare a printing-

out material. This printing-out material immediately developed color by exposure to a mercury lamp to give a deep green image on a white background. The image was then fixed by means of hot drums to obtain a clear and stable image. The fixing of a second imaged sheet of this printing-out material was effected by washing with water to obtain a stable image.

EXAMPLE 3

The above procedures were repeated, except that the photoactivatable component was replaced by the same amount of 2-phenethylbenzothiazole-methyl iodide, to obtain a composition. A printing-out material was prepared from this composition and was subjected to the same treatment as above to give a clear and stable image on a white ground.

EXAMPLE 4

A light-sensitive, printing-out composition was prepared in a dark place according to the following formulation:

2-methylbenzothiazole-ethyl fluoborate—20 g.
Benzoyl acetonitrile—30 g.
Cellulose acetate butyrate—15 g.
Methanol—500 ml.
Ethyl acetate—500 ml.

The thus prepared composition was coated to a thickness of 20 ml./m.^{2} on a photographic baryta paper of 150 g./m.^{2} in thickness and was then dried to obtain a printing-out material. When subjected to printing by use of a mercury lamp, said printing-out material immediately developed color to give a purple clear image on a white ground. The printing-out material had about 2 times the sensitivity of a commercial dry diazotype light-sensitive paper. The image, after printing, was fixed by washing with ethyl acetate to give a stable image high in resolving power.

EXAMPLE 5

The above procedures were repeated, except that in place of the benzoyl acetonitrile employed as a color-formable component was used the same amount of salicylidene-B-naphthylamine, to prepare a printing-out material. The thus prepared printing-out material gave a yellowish brown clear image with good resolution on a white ground.

EXAMPLE 6

A light-sensitive, printing-out composition was prepared in a dark place according to the following formulation:

2-phenethylbenzothiazole-methyl iodide—50 g.
N-nitrosodiphenylamine—50 g.
Methylvinylether-maleic anhydride copolymer—15 g.
Acetone—300 ml.
Methanol—700 ml.

The thus prepared composition was coated in a dark place according to a known procedure on a photographic cellulose triacetate film base and was then dried to obtain a printing-out material. On this printing-out material was placed a microfilm negative, and the composite was subjected to printing by use of a mercury lamp, whereby the material immediately developed color to give a brown color image on a transparent ground. The image was fixed by passing the material between hot rolls having a surface temperature of 140° C., whereby a microfilm positive, with good resolution, suitable for projection could be obtained. When the material is printed in combination with a photographic negative of the ordinary halftone, there is obtained a clear transparent positive excellent in tone quality. Further, the material of this example is suitable for an intermediate original for diazo-copying method.

EXAMPLE 7

50 g. of 2-methylbenzothiazole-methyl iodide was dissolved in 1,000 ml. of a 3% aqueous gelatine solution. To the solution were added 50 g. of benzophenone and 30 g. of white alumina powder, and the mixture was milled for 20 hours in a ball mill to obtain a light-sensitive, printing-out composition, which was a microfine dispersion. The thus obtained composition was coated in a dark place on a photographic baryta paper according to a known procedure, and was then dried to obtain a printing-out material. This printing-out material was subjected to printing by use of a mercury lamp, whereby the material immediately developed color to give a clear brown image on a white ground. The image could be made into a stable image by fixing with hot rolls.

EXAMPLE 8

Two liquids A and B were prepared in a dark place according to the following formulations.
Liquid A:

2-methylbenzothiazole-methyl iodide—40 g.
Sodium fluoride—40 g.
Water—600 ml.

Liquid B:

o-Phthalaldehydic acid—30 g.
Acridine Orange (2% methanol solution)—5 ml.
Water—400 ml.

The two liquids were mixed to prepare a light-sensitive, printing-out composition. The thus prepared composition was coated on a photographic baryta paper according to a known procedure and was then dried to obtain a printing-out material. This printing-out material is extremely high in sensitivity, because it contains the color sensitizer together with the sensitizer sodium fluoride, and hence can give a printed-out image by use of a visible light. A positive clear blue 50× enlargement image was prepared on the printing-out material from a microfilm image using a 300 w. slide projector. When the material was passed between hot drums having a surface temperature of 160° C., the image is fixed to form a stable image, with good resolution, which is not discolored even when directly exposed to sunlight.

EXAMPLE 9

A light-sensitive composition was prepared in a dark place according to the following formulation:

2-methylbenzoselenazole-n-butyl iodide—20 g.
p-Nitrobenzaldehyde—30 g.
Polyvinyl acetate—20 g.
Ethyl acetate—100 ml.

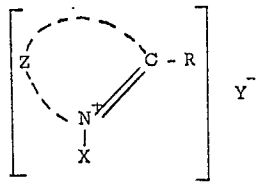
According to a known procedure, the thus obtained composition was coated to a thickness of 25 ml./m.^{2} on a plastics-coated paper, which had been subjected to surface treatment with polyvinyl alcohol, and was then dried to prepare a printing-out material. This printing-out material was treated in the same manner as in Example 1 to give a clear and stable yellowish brown image on a white background. The sensitivity of the material was about 1.6 times higher than that of the material obtained in Example 1.

The above examples have been presented for the purpose of illustration and should not be taken to limit the scope of the present invention. It will be apparent that the described examples are capable of many variations and modifications which are likewise to be included within the scope of the present invention as set forth in the appended claims.

What is claimed is:

1. Light-sensitive reproduction material comprising a support and a light-sensitive composition comprising:

(a) a photoactivatable compound of the general formula:



wherein

R is an alkyl group of 1 to 3 carbon atoms or an aralkyl group;

X is (1) an alkyl group of 1 to 4 carbon atoms, or an aralkyl, with Y as an anion to form a quaternary compound, or (2) a lower alkylene combined with an anion to form an inner salt; and

Z is an atomic group necessary to form a heterocyclic ring system; and

(b) a color-formable compound reactive in conjunction with said photoactivatable compound upon exposure to light to form a distinct color.

2. Material according to claim 1 including a sensitizer selected from the group consisting of cyanine, xanthene, and acrydine compounds.

3. Material according to claim 1 including a heat-active fixing agent selected from the group consisting of nitrites, sulfites, hydrozines, and hydroxylamines.

4. The method of preparing a permanent image comprising:

(a) imagewise exposing material according to claim 1 to actinic radiation for a time sufficient to create a visible color-body image thereon; and

(b) fixing said image.

5. The method according to claim 4 wherein said fixing step includes washing the exposed material with a liquid which is a solvent for said color-formable compound and is a non-solvent for said color-body.

6. The method according to claim 4 wherein said fixing step includes heating said composition to a temperature between about 100° C. and 180° C.

References Cited

UNITED STATES PATENTS

2,811,510 10/1957 Leubner et al. ------- 96—90 X

J. TRAVIS BROWN, Primary Examiner

W. H. LOWE, JR., Assistant Examiner

U.S. Cl. X.R.

96—90