United States Patent Office 3,582,342 Patented June 1, 1971

3,582,342

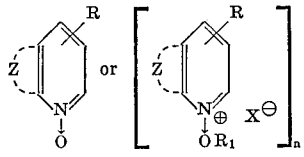
LIGHT-SENSITIVE PHOTOGRAPHIC MATERIALS

Kohei Itano, Hachioji, Masashi Nakano, Tokyo, Akira Kato, Hachioji, and Shoichiro Hoshino, Tokyo, Japan, assignors to Keuffel & Esser Company, Hoboken, N.J.

No Drawing. Filed July 14, 1967, Ser. No. 653,343
Claims priority, application Japan, July 16, 1966, 41/46,257
Int. Cl. G03c 1/52
U.S. Cl. 96—90 12 Claims

ABSTRACT OF THE DISCLOSURE

A photosensitive material useful in copying processes is provided by combining dyes or colorless dye bases with photoactivators selected from N-oxide compounds of pyridine or quinoline, or quaternary salts thereof, having the general formula:



Upon exposure to light the photoactivators provide free radicals which cause a dye-forming or bleaching color change.

BACKGROUND OF THE INVENTION

A variety of so-called printing-out-type light-sensitive materials which develop images by action of light have previously been known. Such materials include silver printing-out type light sensitive materials chiefly containing light-sensitive silver salts; blue print light-sensitive materials mainly containing light-sensitive iron salts; the compositions using organic halogen-containing compounds capable of forming free halogen radicals by action of light, such as disclosed in U.S. Pats. Nos. 3,042,515 to 3,042,519; and compositions containing as light-sensitive components leucocyanides of triphenylmethane dyes, such as set forth in U.S. Pat. No. 2,676,887.

These conventional materials, however, have suffered from such drawbacks that they are relatively expensive, give unstable images which are discolored or faded, generate offensive odors or poisonous vapors or are difficult in handling. For example, the silver printing-out type light-sensitive materials are not only expensive but also are low in speed, and the resulting images are not sufficiently stable, though the images are excellent in contrast. The blue print light-sensitive materials have such defects that the resulting images are poor in contrast, low in speed and insufficient in resolution, though they are excellent in stability. Further, the compositions using organic halogen-containing compounds have suffered from such faults that the photoactive components are extremely poisonous and are volatile and, therefore, prudent care has been required in handling these materials.

The light-sensitive photographic material of the present invention avoids such drawbacks as mentioned above and has excellent overall quality as compared with said conventional photographic materials. As a result, the photographic material of the present invention is convenient to use, and the resulting image is not only excellent in contrast and resolution but also is high in stability.

SUMMARY OF THE INVENTION

The light-sensitive photographic material of the present invention is composed mainly of a photoactivator capable of being made reactive by action of light and which is selected from the group consisting of N-oxide compounds of pyridine and quinoline, or quaternary salts thereof, and a second color-modifier component which shows a visible color change by reaction with the light-activated photoactivator. Arylamine, leuco-form, arylmethane, and azomethine dyes are among the many compounds useful as the second component of the material.

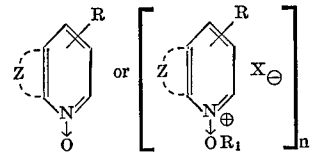
The material of the invention is readily prepared by coating on a support of paper or the like a solution containing the major components and drying the coating. In addition to these two major components, the coating composition may advantageously include binder resins and light sensitizing compounds.

The photographic material of the present invention directly shows a visible change by exposure to ultraviolet light or visible light. Therefore, when the material is placed under a photographic negative or manuscript and is subjected to printing by use of such light, a clear image can be immediately obtained which can subsequently be made into a stable image through fixing operations including heating or dissolving out the active components.

Any of the compounds useful as the components employed in the photographic material of the present invention are non-toxic and stable substances and are obtainable at low costs. Therefore, the present photographic material is not only safe in handling but also is excellent in storability, and can be prepared at low cost.

DESCRIPTION OF THE INVENTION

The first component employed in the present invention is a photoactivator capable of being brought into a reactive state by action of light, and is an N-oxide compound of pyridine or quinoline, or a quaternary salt thereof, which is represented by the general formula



wherein n is an integer of 1 or 2; R is a hydrogen atom or a C_1–C_3 alkyl, aralkyl, halogen, nitrile, mercapto or formyl group; R_1 is a C_1–C_4 alkyl or aralkyl group, or is a C_2–C_4 alkyl or aralkyl group, or is a C_2–C_4 alkylene or xylylene group in case n is 2; X is an anion; and Z is two separate hydrogen atoms, or atomic groups necessary to complete a benzene irng.

Such photoactivators include: N-oxide derivatives such as

pyridine-N-oxide,
α-picoline-N-oxide,
α-benzylpyridine-N-oxide,
α-bromopyridine-N-oxide,
γ-chloropyridine-N-oxide,
α-cyanopyridine-N-oxide,
γ-mercaptopyridine-N-oxide,
quinoline-N-oxide,
quinaldine-N-oxide,
4-bromoquinoline-N-oxide,
2,4-dichloroquinoline-N-oxide,
2-cyano-4-bromoquinoline-N-oxide,
2-bromo-4-cyanoquinoline-N-oxide,
2,4-dimethylquinoline-N-oxide,
2-formylquinoline-N-oxide and
4-formylquinoline-N-oxide.

Useful quaternary salts of N-oxides include

N-benzyloxypyridinium bromide,
N,N'-o-xylylenedioxy-bis-2-methylpyridinium bromide,
N,N'-xylylenedioxy-bis-pyridinium bromide,
N-ethoxy-2,4-dimethylpyridinium iodide,
N-methoxyquinoline iodide,
N-benzyloxyquinolinium bromide,
N,N'-o-xylylenedioxy-bis-2-methylquinolinium bromide,
N,N'-p-xylylenedioxy-bis-quinolinium bromide,
N-ethoxy-4-chloropyridinium iodide,
N-methoxypyridinium iodide,
N-methoxypyridinium-p-toluenesulfonate,
N-methoxy-2-methylpyridinium iodide,
N-methoxy-2-methylpyridinium-p-toluenesulfonate,
N-methoxy-2-bromopyridinium iodide,
N-methoxy-2-bromopyridinium-p-toluenesulfonate,
N-methoxy-4-chloropyridinium iodide,
N-methoxy-4-chloropyridinium-p-toluenesulfonate,
N-methoxyquinolinium iodide,
N-methoxyquinolinium p-toluenesulfonate,
N-methoxy-2-methylquinolinium iodide,
N-methoxy-4-chloroquinolinium iodide,
N-methoxy-2-cyanoquinolinium iodide,
N-ethoxypyridinium iodide,
N-ethoxy-2-methylpyridinium iodide,
N-ethoxy-2-bromopyridinium iodide,
N-ethoxy-2,4-dimethylpyridinium iodide,
N-ethoxy-2-cyano-4-bromopyridinium iodide,
N-ethoxyquinolinium iodide,
N-ethoxy-2-methylquinolinium iodide,
N-ethoxy-4-chloroquinolinium iodide,
N-ethoxy-2-cyanoquinolinium iodide,
N-ethoxy-2,4-dichloroquinolinium iodide,
N-ethoxy-2-bromo-4-cyanoquinolinium iodide,
N-ethoxy-2,6-dimethylpyridinium iodide,
N-butoxypyridinium iodide,
N-butoxy-2-methylpyridinium iodide,
N-butoxy-2,6-dimethylpyridinium iodide,
N-butoxy-2-cyanopyridinium iodide,
N-butoxy-2-bromopyridinium iodide,
N-butoxy-2-cyano-4-bromopyridinium iodide,
N-butoxy-4-chloropyridinium iodide,
N-butoxy-quinolinium iodide,
N-butoxy-2-methylquinolium iodide,
N-butoxy-2,4-dimethylquinolinium iodide,
N-butoxy-2-chloroquinolinium iodide,
N-benzyloxy-2,4-dichloroquinolinium bromide,
N-benzyloxy-2-bromo-4-cyanoquinolinium bromide,
N-benzyloxypyridinium chloride,
N-benzyloxy-2-methylquinolinium chloride,
N-benzyloxy-2,4-dichloropyridinium chloride,
N-p-nitrobenzyloxypyridinium bromide,
N-p-nitrobenzyloxy-2-bromopyridinium bromide,
p-nitrobenzyloxyquinolinium bromide,
p-nitrobenzyloxy-2-methylquinolinium bromide,
p-nitrobenzyloxy-2,4-dichloroquinolium bromide,
N-p-bromophenethyloxypyridinium bromide,
N-p-bromophenethyloxy-2-methylpyridinium bromide,
N-p-bromophenethyloxy-2-bromopyridinium bromide,
N-p-bromophenethyloxyquinolinium bromide,
N-p-bromophenethyloxy-2-methylquinolium bromide,
N-p-bromophenethyloxy-2,4-dibromoquinolium bromide,
N,N'-o-xylylenedioxy-bis-pyridinium bromide,
N,N'-o-xylylenedioxy-bis-2-methylpyridinium bromide,
N,N'-o-xylylenedioxy-bis-2-cyanopyridinium bromide,
N,N'-o-xylylenedioxy-bis-2-bromopyridinium bromide,
N,N'-o-xylylenedioxy-bis-2,6-dimethylpyridinium bromide,
N,N'-o-xylylenedioxy-bis-2-cyano-4-chloropyridinium bromide,
N,N'-o-xylylenedioxy-bis-quinolinium bromide,
N,N'-o-xylylenedioxy-bis-2-methylquinolium bromide,
N,N'-o-xylylenedioxy-bis-2,4-dichloroquinolium bromide,

N,N'-o-xylylenedioxy-bis-2-cyanoquinolium bromide,
N,N'-o-xylylenedioxy-bis-2-cyano-4-chloroquinolium bromide,
N,N'-p-xylylenedioxy-bis-pyridinium bromide,
N,N'-propylenedioxy-bis-pyridinium bromide and
N,N'-butylenedioxy-bis-pyridinium bromide.

Many additional compounds conforming to the above general formulae are similarly useful in the present invention.

These compounds employed as the first components in the present invention do not visibly change by themselves by action of light, but are brought into the form of highly reactive free radicals which cause visible changes by reaction with the second components to bring about basis for image formation.

The second components employed in the present invention in combination with the aforesaid photoactivators, do not cause visible changes by themselves by action of light, as in the case of photoactivators, but cause visible changes by reaction with the photoactivators which have become reactive by action of light. As the second components having such properties, chemical substances of a markedly wide scope may be used and it is thus impractical to exemplify them as substances having structures within a specific scope. In short, however, all such substances which cause visible changes when exposed to light together with the aforesaid photoactivators are useable as the second components in the present invention. Therefore, in selecting the second components, there may be employed the following simple test method. A substance desired to be used and any of the aforesaid photoactivators are dissolved together in an appropriate solvent. The solution is applied to a piece of paper, and the paper is dried and is then exposed to light. If the paper shows a visible color change, the tested substance is useable as the second component in the present invention.

Compounds which have been found to be effective as the second components according to the above test method are classified into two types; one involves substances which are originally colorless, but develop a distinct color by action of free radicals generated from the photoactivators, and the other involves substances which originally have a distinct color, but may be decolored or bleached by action of the free radicals. A light sensitive photographic material prepared by using the former type as the second component is originally colorless, but develops color by action of light and hence is used in a so-called negative-positive process, while a photographic material prepared by using the latter type is used in a positive-positive process. Typical as the second components belonging to the former type are arylamines including, in addition to the ordinary arylamines, so-called leuco coloring matters which are reduced types of coloring matters having amino groups or substituted amino groups. Examples of such components are

diphenylamine,
p-oxydiphenylamine,
p-benzoyloxydiphenylamine,
dibenzylamine,
N,N'-diethylaniline,
N-hydroxy-N-ethylaniline,
N,N'-dihydroxydiethylaniline,
dibenzylaniline,
o-aminodiphenylamine,
phenylindolizine,
phenylindole,
p,p'-methylenebis-aniline,
p,p'-methylenebis-(N,N'-dimethylaniline),
p,p'-benzylidenebis-(N,N'-diethylaniline),
p,p',p''-methylidinetris-(N,N'-diethylaniline),
p,p'-hydroxymethylene-bis-(N,N'-dimethylaniline),
p,p'-(dimethylamino)-diphenylamine,
p,p'-aminomethylenebis-(N,N'-dimethylaniline),

p,p'-(o''-chlorobenzylidene)-bis(N,N'-dimethylaniline),
p,p'-(p''-aminobenzylidene)-bis-aniline,
p,p'-(p''-amino-m''-methylbenzylidene)-bis-(N-phenylaniline),
1,1-bis-(p-dimethylaminophenyl)-p-dimethylaminophthalein,
3,6-bis-(diethylamino)-spiro-(phthalein-1,9-xanthene),
3,6-bis-(diethylamino)-9-(p-dimethylaminophenyl)-xanthene,
1,1-bis-(p-dimethylaminophenyl)-p-dimethylaminophthalan,
1,1-bis-(p-aminophenyl)-p'-aminophenylphthalan,
10-benzoyl-3,7-di-(p-dimethylamino)-phenothiazine and
3-diethylamino-7-aminophenoxazine.

Further, as the substances employed in the positive-positive process which originally have a distinct color, but are discolored or decolored by action of free radicals, there are effectively used various dyes of the diphenylmethane, triphenylmethane, thiazine, oxazine, xanthene, anthraquinone, iminonaphthoquinone and azomethine types. Examples of such coloring matters are Auramine (C.I. 41,000), Victoria Blue (C.I. 44,045), Victoria Blue R (C.I. 44,040), Brilliant Roseaniline Blue R (C.I. 42,565), Benzoyl Methylene Blue Cinnamoyl Methylene Blue, New Methylene Blue (C.I. 51,195), Nile Blue A (C.I. 51,180), Ephitenew Blue (C.I. 51,185), Rhodamine B (C.I. 45,170), Rhodamine 3B (C.I. 41,175), Rhodamine 12GM (C.I. 45,310), Suden Blue G (C.I. 61,520), Celliton Blue (C.I. 64,500), 4 - p - diethylaminophenylimino - naphthoquinone, 2-carboxyanilino - 4 - p - diethylamino - phenyliminonaphthaquinone, 2 - carbostearylamino - 4 - p - dihydroxyethylaminophenylimino - naphthoquinone, p - methoxybenzoyl - p' - diethylaminophenyliminoacetanilide and cyano-p-diethylaminophenyliminoacetanilide.

The light-sensitive photographic material of the present invention, which is composed of the above-mentioned photoactivator and the second component, is preferably obtained by dissolving the components in a solvent together with a suitable high molecular weight binder having a film-forming property, and applying the solution to a suitable support such as paper of film base, followed by drying.

As the high molecular weight binders useable in the above case, there are various compounds including, for example, cellulose derivatives such as acetyl cellulose, acetylbutyryl cellulose and ethyl cellulose, polymers and copolymers of vinyl chloride, vinylidene chloride, vinyl acetate, acrylate and styrene, styrene-maleic anhydride copolymer, and synthetic rubbers such as cyclized rubbers, acryl rubbers and butadiene copolymers.

The color change in the photographic material of the present invention is due to a free radiacl formed from the photoactivator by action of light, particularly ultraviolet light. The light sensitivity of the present photographic materials can further be enhanced by addition of suitable sensitizers. As such sensitizers, there are two kinds; those belonging to so-called color sensitizers which broden the light-sensitive wave length area of the photographic materials to increase the light sensitivity thereof and those belonging to true sensitizers which increase the light sensitivity regardless of the light-sensitive wave length area.

As the sensitizers belonging to the former, there are effectively used acridine, cyanine, merocyanine and styrene dyes which have been employed as light-sensitive coloring matters in the conventional silver salt photographic method. Examples of these are Acridine Orange, Acridine Red, Rose Bengal, pinacyanol, pinakryptol yellow,
1-[3-ethyl-2(3H)-benzothiazolylidene]-4-butylidene-dibenzothiazolymethane,
1-[ethyl-4-(1H)-quinolidene]-ethylidene-di-2-benzothiazolylmethane,
5,2-(3-ethylbenzoxazolidene)-ethylidene-2-phenylimide-3-phenyl-4-keto-tetrahydrothiazole,
1,3-diethylthio-4-carbocyanineiodide,
1,3-dimethyloxa-2'-carbocyanine-p-toluenesulfonate and
5,1-methyl-2-(1H)-quinolidene-2-butylidene-3-ethyl-2-thio-2,4-oxazolidenedione.

As the true sensitizers belonging to the latter, there are effectively employed, in general, such aldehydes as, for example, benzaldehyde, dimethylaminobenzaldehyde, orthophthalodialdehyde, salicylaldehyde, anisaldehyde, phenylacetaldehyde, ascorbic acid, benzaldehyde-sulfonic acid and succinaldehyde.

By the proper use of the noted sensitizers, the light sensitivity of the present photographic materials can be increased manyfold.

The photographic material of the present invention is fixed, after printing, by being subjected to either heating or solvent treatment. In case the photographic material is to be heat fixed, the incorporation of a heat fixing agent promotes the fixing effect and a stable image can be more readily obtained. Effective as such heat fixing agents are urea and urea derivatives such as methylurea, ethylurea, diphenylurea and thiourea, sodium sulfite or bisulfite and aldehyde or ketone addition products such as, for example, rongalite, sodium bisulfite-benzaldehyde addition product and sodium bisulfite-cyclohexanone addition product, and reducing compounds such as stannous chloride. The heat fixing agent is incorporated into a binder solution together with photoactivator and color modifier. If the heat fixing agent employed is insoluble in the binder solution, it is formed into an aqueous solution at a concentration of about 0.5–5% and is applied onto the surface of the light-sensitive layer of the present photographic material.

The photographic material of the present invention is obtained by dissolving the above-mentioned components in a binder solution and applying, according to any common procedure, the thus prepared solution onto a suitable support. In this case, preferable quantitative proportions of the individual components are as follows:

	Parts by weight
Solvent	500–1000
Film-forming binder	20–100
Photoactivator	5–50
Color modifier	10–100
Heat fixing agent (optical)	5–10
Sensitizer (optional)	1–5

As the support, any paper, plastics film base, glass plate and metal plate may be used. Generally, however, the use of photographic papers and plastics-coated papers makes it possible to obtain clear images excellent in resolution and high in density. The thickness of the light-sensitive layer to be formed on the support is most preferably about 1–3μ, in general, though the sensitivity increases and the density becomes high with increasing thickness.

When the present light-sensitive photographic material obtained in the manner as explained above is subjected to printing by exposure to light, such as by placing an original image thereon, a color is immediately developed or the coloring matter is discolored or decolored to give a clear image. The light sensitivity of the present photographic material is generally many times higher than that of the diazo sensitive paper commercially available at present. If necessary, an enlarged image of an original may also be obtained by use of a suitable projection means. The image formed by printing is stable, but cannot be preserved in a bright place unless the light sensitivity of unexposed areas is removed. Therefore, the image should be subjected to fixing.

The fixing is effected in such a manner that the material after printing is either heated to stabilize the residual photoactivator and color modifier, or is treated with a suitable solvent to remove such components. The heat fixing is simply carried out by passing the material between rolls heated a surface temperature of about 150–

180° C. For the solvent fixing, there is selected and used such a suitable solvent as to dissolve the photoactivator without dissolving the coloring matter formed by exposure to light or the coloring matter remaining without being discolored or decolored. For example, a solvent comprising a 50:50 mixture of ethyl acetate and cyclohexane is most suitable for a negative-positive type photographic material using the previously cited α-bromopyridine-N-oxide as a photoactivator and diphenylamine as a color modifier, and gasoline is most preferable for a photographic material using N-methoxy-2-methylquinolinium iodide as a photoactivator and Lucocrystal Violet as a color modifier. Such solvents as trichloroethylene, methanol and acetone dissolve out color images formed and hence are not usable. Thus, in effecting the solvent fixing, it is necessary to select a suitable solvent according to the constituents of the photographic material employed. It is sufficient to effect the solvent fixing treatment for 0.5–2 minutes in the presence of a suitable solvent. By this treatment, the image formed becomes stable and causes no change even when held in a bright place.

PREFERRED EMBODIMENTS

Example 1

A photographic paper, which had been subjected to surface treatment by application of 1–1.5 g./m.² of polyvinyl alcohol having a polymerization degree of about 600, was coated under a yellow safety lamp with 30 cc./m.² of a light-sensitive solution having the following composition and dried to obtain a light-sensitive photographic material:

α-Bromopyridine-N-oxide—10 g.
Diphenylamine—10 g.
Saran F–220 (vinylidene chloride-acrylonitrile copolymer resin produced by Dow Chemical Co.)—5 g.
Acetone—100 cc.

On the thus obtained light-sensitive photographic material, a photographic negative was placed, and the material was exposed for 5 seconds to an 800 w. mercury lamp positioned at a distance of 5 cm. from the material to obtain a deep blue positive image on a white background. This image was subjected to solvent fixing by immersing the material for one minute in a 50:50 mixed solution of ethyl acetate and cyclohexane, whereby the image was made entirely stable against exposure to light. Even when compared with a commercially available diazo copying paper, the thus prepared photographic material was favorable in sensitivity, markedly excellent in resolution and distinct in hue. Further, the same result as above was obtained, as well, when N-ethoxy-2-bromopyridinium iodide was used in place of the -bromopyridine-N-oxide.

Example 2

A light-sensitive photographic material was prepared by use of a light-sensitive solution having the following composition:

α-Methylpyridine-N-oxide—10 g.
Leucocrystal violet—2 g.
Saran F–220—5 g.
Acetone—100 cc.

The photographic material was subjected to the same treatment as in Example 1 to obtain a clear, deep purple image on a white background.

Further, the same result as above was obtained, as well, when N-benzyloxy-2-methylpyridinium bromide was used in place of the α-methylpyridine-N-oxide.

Example 3

A sensitizer-containing light-sensitive solution was prepared according to the following:

2-bromoquinoline-N-oxide—10 g.
2-phenylindolizine—10 g.
4-dimethylaminobenzaldehyde—2 g.
Cellulose acetate—10 g.
Acetone—30 cc.
Benzene—70 cc.

According to common procedures and under a yellow safety lamp, the above composition was applied in a proportion of 20 cc./m.² onto a 0.14 mm. thick cellulose triacetate film base, and the coated film was dried in a dark place at a temperature below 60° C. to obtain a light-sensitive photographic material. This photographic material was imagewise exposed for 2 seconds to the same light as in Example 1 to develop a clear greenish blue image.

Thus, the light-sensitive photographic material of this example can give an image of sufficient density even when exposed to light for a markedly short period of time.

Further, the same result as above was obtained, as well, when N-butoxy-2-bromoquinolinium iodide was used in place of the 2-bromoquinoline-N-oxide.

Example 4

The same photographic original sheet as used in Example 1 was coated with 30 cc./m.² of a light-sensitive solution having the composition shown below and was then dried to prepare a light-sensitive photographic material.

2,4-dibromoquinoline-N-oxide—10 g.
2-chloro-4-(4′-diethylaminophenyl)-imino-naphthoquinone—2 g.
Cellulose acetate—10 g.
Acetone—50 cc.
Methanol—50 cc.

This photographic material was exposed to the same light as in Example 1 to obtain a clear, white, decolored image on a blue background. When material was immersed in gasoline for 2 minutes, the image was completely fixed even to exposure to strong ultraviolet light.

Further, the same result as above was obtained, as well, when N,N′-ethylenedioxy-bis-2,4-dibromoquinolinium bromide was used in place of the 2,4-dibromoquinoline-N-oxide.

Example 5

The same photographic paper as used in Example 1 was coated with 30 cc./m.² of a light-sensitive solution having the composition shown below and was then dried to prepare a light-sensitive photographic material.

4-formylquinoline-N-oxide—10 g.
Leuco-malachite green—2 g.
Urea—3 g.
Cellulose acetate—5 g.
Methanol—50 cc.
Acetone—50 cc.

This photographic material was imagewise exposed to the same light as in Example 1 to obtain a clear green image on a white background. The image-bearing material was heated for 2 seconds between rolls having a surface temperature of 150° C., the image was completely fixed even to exposure to strong ultraviolet light.

Further, the same result as above was obtained, as well, when N,N′-ethylenedioxy-bis-2,4-dibromoquinolinium bromide was used in place of the 4-formylquinoline-N-oxide.

Example 6

The same photographic paper as used in Example 1 was coated with 35 cc./m.² of a light-sensitive solution having the composition as shown below and was then dried to prepare a light-sensitive photographic material.

2-cyano-4-bromoquinoline-N-oxide—10 g.
Leuco-opal Blue—2 g.
1,1′-dimethyl-2,2′-dicarbocyanine-p-toluenesulfonate—0.05 g.
Nitrocellulose—10 g.
Acetone—50 cc.
Methanol—50 cc.

This photographic material was imagewise exposed to light at a distance of 15 cm. for 10 seconds by use of a slide projector having a 500 w. cine-projecting tungsten bulb as a light source, whereby a clear blue image was obtained. The image-bearing material was immersed either in gasoline for 2 minutes, or in a 10% aqueous rongalite solution for 1–2 seconds, and was then dried to obtain an image which was even when exposed to strong ultraviolet light.

Further, the same result as above was obtained, as well, when N,N'-p-xylylenedioxy-bis-2-bromopyridinium bromide was used in place of the 2-cyano-4-bromoquinoline-N-oxide.

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:

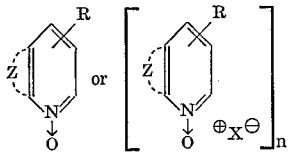
1. Light-sensitive photographic material comprising a support and a composition comprising:

(a) a photoactivator capable of forming a free radical upon exposure to light; and

(b) a color-modifier capable of reacting under the influence of said free radical to provide a distinct color change,

(c) said photoactivator being an N-oxide compound of the general formula:

wherein



n is an integer of 1 or 2;

R is a hydrogen atom or a C_1 to C_3 alkyl, aralkyl, halogen, nitrile, mercapto or formyl group;

R_1 is a C_1 to C_4 alkyl or aralkyl group or, where n is 2, a C_2 to C_4 alkylene or xylylene group;

X is an anion; and

Z is two separate hydrogen atoms, or atomic groups necessary to complete a benzene ring.

2. Material according to claim **1** wherein said color-modifier is a compound capable of forming a distincely visible color-body in the presence of said free radicals.

3. Material according to claim **2** wherein said color-modifier is selected from the group consisting of arylamines and leuco bases.

4. Material according to claim **1** wherein said color-modifier is a visibly colored compound capable of being converted to a distinctly different color in the presence of said free radicals.

5. Material according to claim **4** wherein said color-modifier is selected from the group of dyes consisting of derivatives of diphenylmethane, triphenylmethane, thiazine, oxazine, xanthene, anthraquinone, iminonaphthoquinone, and azomethine.

6. Material according to claim **1** wherein said composition includes up to about 50% by weight of a film-forming binder resin.

7. Material according to claim **1** wherein said composition includes up to about 20%, based on the photoactivator, of a light sensitizer selected from the group consisting of color sensitizing dyes and aldehydric spectra sensitizers.

8. Material according to claim **1** wherein said composition includes heat fixing agent selected from the group consisting of urea, urea derivatives, sodium sulfite, bisulfite adducts of aldehydes and ketones, and stannous reducing agents.

9. A method of forming a permanent image comprising:

(a) imagewise exposing to light material according to claim **1** for a time sufficient to produce a visible color change therein; and

(b) treating the thus-exposed material to render the photoactivator in the unexposed of said material inactive to light exposure.

10. The method of claim **9** wherein said treating step comprises contacting said unexposed with a solvent for said photoactivator.

11. The method of claim **9** wherein said treating step comprises heating said material to a temperature between about 150°–180° C.

12. A method of forming a permanent image comprising:

(a) imagewise exposing to light material according to claim **8** for a time sufficient to produce a visible color change therein; and

(b) heating said material to a temperature between about 150°–180° C.

References Cited

UNITED STATES PATENTS

2,426,894	9/1947	McQueen	96—48
3,203,802	4/1962	Burg	96—87
3,305,361	2/1967	Gaynor et al.	96—48

OTHER REFERENCES

Chem. Soc. J., pt. C, 1966, p. 2295, Kaminsky L. S., "Photolysis of Cyclic Nitrones."

J. Org. Chem., vol. 23, 1958, p. 651, Splitter "Preparation of Oxaziranes by Irradiation of Nitrones."

NORMAN G. TORCHIN, Primary Examiner

J. L. GOODROW, Assistant Examiner

U.S. Cl. X.R.

96—48

Notice of Adverse Decision in Interference

In Interference No. 98,526 involving Patent No. 3,582,342, K. Itano, M. Nakano, A. Kato and S. Hoshino, LIGHT-SENSITIVE PHOTOGRAPHIC MATERIALS, final judgment adverse to the patentees was rendered Nov. 28, 1975, as to claims 2, 3, 6, 9 and 11.

[*Official Gazette March 23, 1976.*]