Feb. 2, 1971 HARUO HORI ET AL 3,560,216
LIGHT SENSITIVE FREE RADICAL IMAGING MATERIAL
CONTAINING PYRAZOLINE SENSITIZERS
Filed Dec. 15, 1967

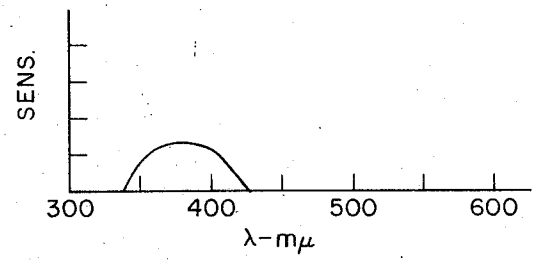


FIG. 1

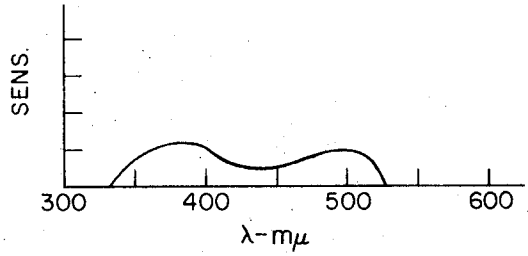


FIG. 2

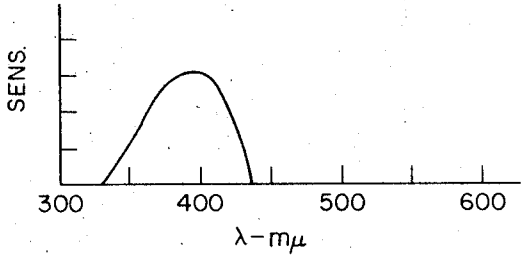


FIG. 3

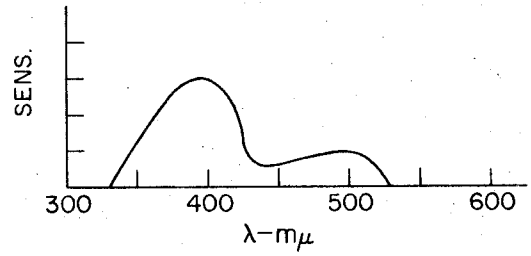


FIG. 4

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United States Patent Office

3,560,216

Patented Feb. 2, 1971

3,560,216

LIGHT SENSITIVE FREE RADICAL IMAGING MATERIAL CONTAINING PYRAZOLINE SENSITIZERS

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Filed Dec. 15, 1967, Ser. No. 690,898

Claims priority, application Japan, Dec. 16, 1966, 41/82,266

Int. Cl. G03c 1/72

U.S. Cl. 96—90 1 Claim

ABSTRACT OF THE DISCLOSURE

Light-sensitive imaging materials comprising color modifiers which visibly change in color or shade in the presence of free radicals in combination with photoactivators which yield free radicals upon exposure to actinic light are substantially increased in light-sensitivity by the addition of an aryl-substituted pyrazoline compound. Such sensitizers are particularly effective in increasing the rate of image-forming reaction with respect to normal spectral ranges rather than in broadening the band of spectral response of such materials.

BACKGROUND OF THE INVENTION

It is known that in a conventional process for sensitizing imaging material comprising color modifiers and light-sensitive photoactivators yielding free radicals on light exposure there is used, for the purpose of increasing the spectral sensitivity of the material, a light sensitive coloring matter such as a dye of the acridine, cyanine, merocyanine or styryl type. Imaging materials of this general type have been widely described, for example in U.S. Pats. 3,042,515 to 3,042,519; 3,102,027 and 3,102,810. Such a sensitizing process, however, is employed in order to broaden the effective wavelength band response of a printing material and aims at the sensitization for a visible zone. Accordingly, the process may be effectively applied to the case where there is used a tungsten lamp which emits a large amount of visible light, but cannot display successful sensitizing effects in the case of a commercially available diazo copying machine in which ultraviolet light is utilized.

Further, according to the above sensitizing process, since a visible zone is sensitized, the room lamps employed at the time of production and printing operation of imaging materials are restricted in wavelength, with the result that the convenience of use is undesirably lowered. In addition, there are brought about such drawbacks that the background of a printing material is greatly stained due to coloration of the light-sensitive coloring matter itself, which is used as a sensitizer, whereby the practical value and photographic quality of the material is lowered.

SUMMARY OF THE INVENTION

The present invention is entirely different in object, structure and effect from such sensitizing process as mentioned above. That is, the present method uses a pyrazoline compound, represented by the general formula shown later, in a free-radical type imaging material to increase the sensitivity of a light sensitive system within the light-sensitive wavelength area inherent to the photoactivator employed (ordinarily 350–420 mμ). Thus, in accordance with the present invention, only the sensitivity in the light-sensitive wavelength area inherent to a light-sensitive system is increased, and therefore particularly prominent effects can be attained in the case where

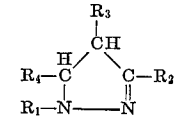
there are used commercially available diazo copying machines and the like ultraviolet printing machines.

When the present method is employed, printing materials, which have not been able to be printed except from an expensive mercury lamp light source, can be printed at a practical speed by use of a fluorescent lamp light source, and the costs of printing light source and the like can be reduced. A mercury lamp does not become stable unless several minutes have elapsed after lighting and cannot be used immediately after lighting, whereas a fluorescent lamp becomes stable simultaneously with lighting and can be advantageously used immediately after lighting. According to the present method, therefore, not only the costs of printing light source can be reduced but also the printing operations can be carried out efficiently.

Further, the light-sensitive wavelength area of the printing material of the present invention is in the ultraviolet zone, as mentioned above, and the room lamps employed at the time of production and printing of the printing material may be covered with filters which can shield only ultraviolet light, whereby the operations can be safely effected in considerably bright rooms.

The pyrazoline compounds employed in the present method are colorless or slight yellow, and there is little danger that the backgrounds of printing materials will be colored and stained or the qualities thereof will be degraded.

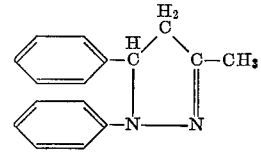
The pyrazoline compounds to be employed in the present invention are those which are represented by the general formula



wherein R_1 is an aryl group; R_2 is a hydrogen atom, alkyl group or aryl group; R_3 is a hydrogen atom, alkyl group or aryl group; and R_4 is a hydrogen atom, aryl group or hetero ring. Examples of these compounds are as follows:

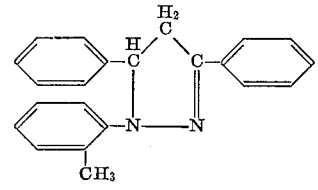
1,5-diphenyl-3-methyl-pyrazoline

(I)



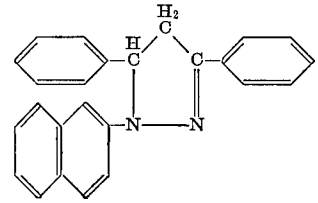
1-o-tolyl-3,5-diphenyl-pyrazoline

(II)

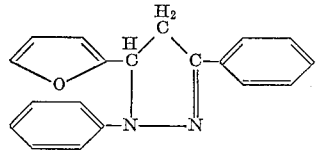


1-β-naphthyl-3,5-diphenyl-pyrazoline

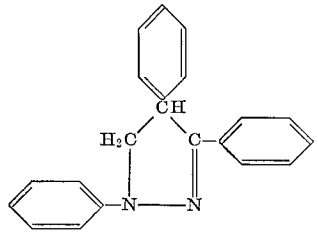
(III)



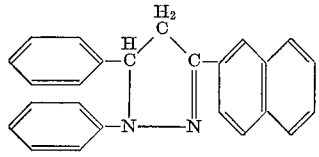
(IV) 1,3-Diphenyl-5-furyl-pyrazoline



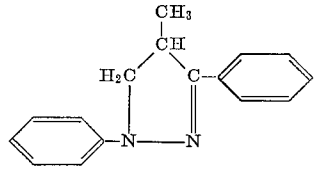
(V) 1,3,4-Triphenyl-pyrazoline



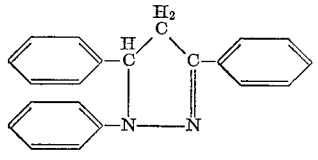
(VI) 1,5-Diphenyl-3(β)-naphthyl-pyrazoline



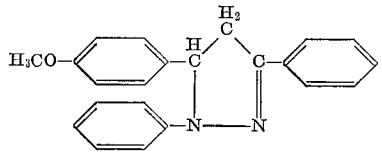
(VII) 1,3-Diphenyl-4-methyl-pyrazoline



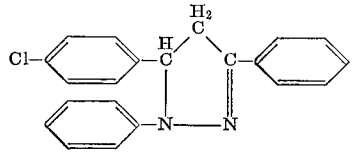
(VIII) 1,3,5-Triphenyl-pyrazoline



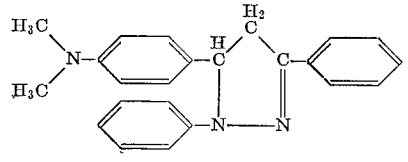
(IX) 1,3-Diphenyl-5-(p-methoxyphenyl)-pyrazoline



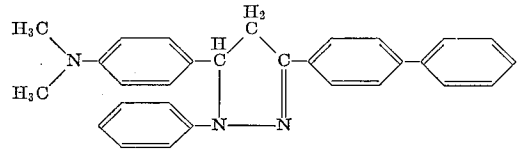
(X) 1,3-Diphenyl-5-(p-chlorophenyl)-pyrazoline



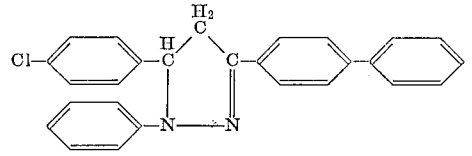
(XI) 1,3-Diphenyl-5-(p-dimethylaminophenyl)-pyrazoline



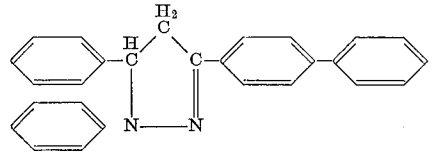
(XII) 1-Phenyl-3-diphenyl-5-(p-dimethylaminophenyl)-pyrazoline



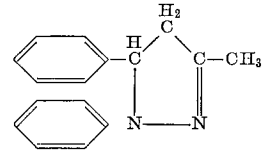
(XIII) 1-Phenyl-3-diphenyl-5-(p-chlorophenyl)-pyrazoline



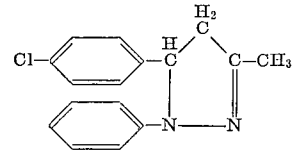
(XIV) 1,5-Diphenyl-3-diphenyl-pyrazoline



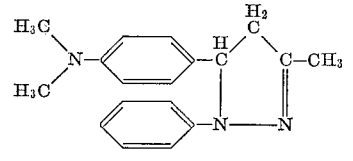
(XV) 1,5-Diphenyl-3-methyl-pyrazoline



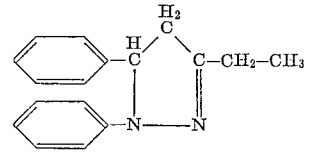
(XVI) 1-Phenyl-3-methyl-5-(p-chlorophenyl)-pyrazoline



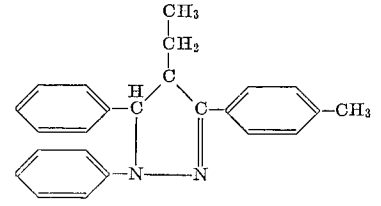
(XVII) 1-Phenyl-3-methyl-5-(p-dimethylaminophenyl)-pyrazoline



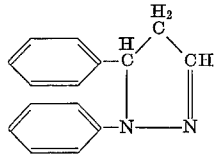
(XVIII) 1,5-Diphenyl-3-ethyl-pyrazoline



(XIX) 1,5-Diphenyl-3-(p-methylphenyl)-4-ethyl-pyrazoline



(XX) 1,5-Diphenyl-pyrazoline



The photoactivators to be used in the light-sensitive printing materials of the present invention, i.e. photoactivators capable of yielding free radicals by action of light, may be any of those which have been known heretofore. Typical examples of such photoactivators are as follows:

(A) Compounds represented by the general formula

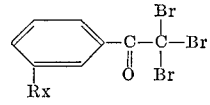
$$R—CX_3$$

wherein R is a hydrogen atom, halogen atom or aryl group; and X is a halogen atom.

These include, for example:

Carbon tetrachloride
Carbon tetrabromide
p-Nitrobenzotribromide
Bromotrichloromethane
Hexabromoethane
Benzotrichloride
Iodoform
1,1,1-tribromo-2-methyl-2-propanol
1,1,2,2-tetrabromoethane
2,2,2-tribromoethanol
1,1,1-trichloro-2-methyl-2-propanol.

(B) Compounds represented by the general formula



wherein R*x* represents 1–5 substituents on the benzene ring which substituents are selected from the group consisting of nitro, halogen, alkyl, haloalkyl, acetyl, haloacetyl, alkaryl and alkoxy groups, and not all of these substituents are required to be same.

These include, for example:

o-Nitro-α,α,α-tribromoacetophenone
m-Nitro-α,α,α-tribromoacetophenone
p-Nitro-α,α,α-tribromoacetophenone
α,α,α-Tribromoacetophenone
α,α,α-m-Tetrabromoacetophenone
α,α,α-Tribromo-3,4-dichloroacetophenone
α,α,α-p-Tetrabromoacetophenone
α,α,α,α′,α′,α′-Hexabromo-p-diacetylbenzene

(C) Compounds represented by the general formula

$$R—SO_2—X$$

wherein R is an alkyl or aryl group which may have a substituent; and X is a halogen atom.

These include, for example:

1,3-benzene disulfonyl chloride
2,4-dinitrobenzenesulfonyl chloride
o-Nitrobenzenesulfonyl chloride
n-Nitrobenzenesulfonyl chloride
3,3′-diphenylsulfone disulfonyl chloride
Ethanesulfonyl chloride
p-Bromobenzenesulfonyl chloride
p-Nitrobenzensulfonyl chloride
p-Iodobenzenesulfonyl chloride
p-Acetamidobenzenesulfonyl chloride
p-Chlorobenzenesulfonyl chloride
p-Toluenesulfonyl chloride
Methanesulfonyl chloride
Benzenesulfonyl chloride
m-Nitrobenzenesulfonyl fluoride
Benzenesulfonyl bromide

(D) Compounds represented by the general formula

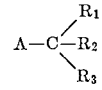
$$R—S—X$$

wherein R is an alkyl or aryl group which may have a substituent; and X is a halogen atom.

These include, for example:

2,4-dinitrobenzenesulfenyl chloride
o-Nitrobenzenesulfenyl chloride

(E) Compounds represented by the general formula

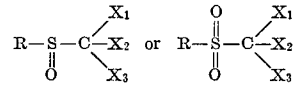


wherein A is a heterocyclic compound residue which may have a substituent; and R_1, R_2 and R_3 are selected from the group consisting of hydrogen, chlorine and bromine atoms, and not all of them are hydrogen atoms at a same time.

These include, for example:

ω,ω,ω-Tribromoquinaldine
ω,ω-Dibromoquinaldine
2-ω,ω,ω-tribromomethyl-4-methylquinoline
ω,ω-Dichloromethyl-quinoline
ω-Bromolepidine
2-ω-bromomethyl-isoquinoline
α-ω,ω,ω-Tribromomethyl-4-chloropyridine
1-methyl-2-chloromethyl-benzimidazole
2,5-ditrobromomethyl-3,4-dibromothiophene

(F) Compounds represented by the general formula



wherein R is a substituted or unsubstituted aryl or heterocyclic residue; and X_1, X_2 and X_3 are selected from the group consisting of hydrogen, chlorine and bromine atoms, and not all of them are hydrogen atoms at a same time.

These include, for example:

Hexabromodimethyl sulfoxide
Pentabromodimethyl sulfoxide
Hexabromodimethyl sulfone
Trichloromethylphenyl sulfone
Tribromomethylphenyl sulfone
Trichloromethyl-p-chlorophenyl sulfone
Tribromomethyl-p-nitrophenyl sulfone
2-trichloromethylbenzothiazolyl sulfone-(2)
4,6-dimethylpyrimidyl-2-tribromomethyl sulfone
Tetrabromodimethyl sulfone
2,4-dichlorophenyl-trichloromethyl sulfone
2-methyl-4-chlorophenyl-trichloromethyl sulfone
2,5-dimethyl-4-chlorophenyl-trichloromethyl sulfone
2,4-dichlorophenyl-tribromomethyl sulfone

As the color modifiers, there are those usable as the so-called negative-positive type which originally are colorless substances but are convertible into a colored state by action of free radicals formed from the above-mentioned photoactivators, and those usable as the so-called positive-positive type which originally are colored substances but are changed in color or are decolored to colorless by action of the free radicals. As these color modifiers, various coloring matters are effectively used, including, for example, amine compounds such as diphenylamine, benzylamine, triphenylamine, N-hydroxyethyl-N-ethylaniline and p,p′-methylenebis (N,N-diethylaniline); leuco bases of dyes such as leuco-malachite green, Michler's hydrol and Leucomethylene Blue; and various dyes of the diphenylmethane, triphenylmethane, thiazine, oxazine, xanthene, anthraquinone, iminonphthoquinone and azomethine types.

The method of the present invention is effectively applied not only to printing materials in which have been

used other known sensitizers, but also to printing materials incorporated with color tone improvers, extenders and binder resins which have heretofore been used in this kind of printing materials.

DESCRIPTION OF DRAWINGS

The drawings show typical spectral sensitivity curves for common free radical imaging materials and free radical materials sensitized according to the present invention.

FIG. 1 relates to unsensitized material.

FIG. 2 relates to material sensitized according to prior art.

FIGS. 3 and 4 relate to material sensitized according to the present invention.

PREFERRED EMBODIMENTS

The present invention concerns means for sensitizing a light-sensitive printing material, characterized by adding to the light-sensitive system a pyrazoline compound represented by the aforesaid general formula. The effective amount of said pyrazoline compound to be added is at least 0.001 part by weight per part of the photoactivator, and favorable results can be obtained when the pyrazoline compound is added in substantially the same amount as that of the photoactivator.

In the present invention, fixing and the like treatments may be effected in the same manner as in the case of the convention printing materials.

In short, the characteristics of the present invention reside in that the pyrazoline compound added to a light-sensitive system makes it possible to shorten the time of printing with ultraviolet light and to effect printing by use of a weak light source without coloring the background of the printing material.

The following examples illustrate preferred embodiments of the present invention:

Example (1)

Light-sensitive compositions shown below were individually applied onto a photographic baryta paper and were dried.

(a) Composition for a known unsensitized light-sensitive material:

Tribromomethylphenyl sulfone—10 g.
Diethanolaniline—30 g.
Acetone—500 cc.
Methanol—500 cc.

(b) Composition of light-sensitive material sensitized with a known sensitizing compound:

Tribromomethylphenyl sulfone—10 g.
Diethanolaniline—30 g.
Acridine orange—5 g.
Acetone—500 cc.
Methanol—500 cc.

(c) Composition of light-sensitive material employed in the present invention:

Tribromomethylphentyl sulfone—10 g.
Diethanolaniline—30 g.
1,3-diphenyl-5-(p-methoxyphenyl)-pyrazoline
(Sensitizer IX)—5 g.
Acetone—500 cc.
Methanol—500 cc.

(d) Composition of light-sensitive material using known sensitizing coloring matter in combination with a sensitizer of the present invention:

Tribromomethylphenyl sulfone—10 g.
Ethanolaniline—30 g.
1,3-diphenyl-5-(p-methoxyphenyl)-pyrazoline
(Sensitizer IX)—5 g.
Acridine orange—5 g.
Acetone—500 cc.
Methanol—500 cc.

The thus obtained light-sensitive printing materials were individually attached with a photographic negative and were exposed for 3 seconds to an 800 w. high pressure mercury lamp at a distance of 5 cm., whereby the materials (c) and (d) gave deep blue positive images whereas the materials (a) and (b) gave mere light blue positive images.

The light-sensitive printing materials bearing individual images obtained in the above were dipped for one minute in a fixing solution of the composition shown below, whereby copies entirely stable to light were obtained. However, the backgrounds of the copies using the materials (b) and (d) were colored to orange to injure the photographic qualities of the copies, whereas the background of the copy using the present material (c) was white without being colored or stained.

Composition of fixing solution:

Stannous chloride	5 parts by wt.
Hydrochloric acid	1 part.
Water	50 parts.

The sensitivity spectra of individual light-sensitive printing materials in this example will be illustrated with reference to the drawings.

FIGS. 1 to 4 show, respectively, the sensitivity spectra of printing materials coated with the light-sensitive emulsions of the compositions (a) to (d) which were used in this example.

FIG. 1 is the sensitivity spectrum of the unsensitized light-sensitive printing materal.

FIG. 2 is the sensitivity spectrum of the light-senstive printing material sensitized according to a known sensitizing process. As is clear from the spectrum, the material was made light-sensitive over a broader wavelength band. In contrast to this, the printing material in accordance with the present invention was increased only in the sensitivity of inherent light-sensitive wavelength area, as seen in the spectrum of FIG. 3. However, the printing material using, in combination, a sensitizer according to the present invention and that employed in the known process was not only increased in the sensitivity of inherent light-sensitive wavelength area but was also broadened in the light-sensitive wavelength band. Thus, it is not objectionable at all to use the sensitizers of the present invention in combination with known sensitizers.

Example (2)

Under a red safety lamp, a light-sensitive composition shown below was applied onto a photographic baryta paper and was dried.

Hexabromodimethyl sulfone—10 g.
Diphenylamine—30 g.
1,3-diphenyl-5-(p-methoxyphenyl)-pyrazoline
(Sensitizer IX)—5 g.
Acetone—500 cc.
Methanol—500 cc.

The thus obtained light-sensitive printing material was attached to a photographic negative and was exposed for 3 seconds to an 800 w. high pressure mercury lamp at a distance of 5 cm., whereby a deep blue positive image with a white background was immediately obtained.

The printing material bearing said image was dipped for one minute in a fixing solution of the following compositions to obtain a copy entirely stable to light.

	Parts
Stannous chloride	5
Hydrochloric acid	1
Water	50

On the other hand, a control material, prepared according to the above formulation from which the sensitizer, compound IX, had been excluded, required 15 seconds in obtaining a positive image of the same intensity by exposure under the same conditions as above.

Example (3)

In the same manner as in Example (2), a light-sensitive composition shown below was applied onto a photographic baryta paper.

Tribromomethylphenyl sulfone—10 g.
Diethanolaniline—30 g.
1-phenyl-3-diphenyl-5-(p-dimethyl-aminophenyl)-pyrazoline (Sensitizer XII)—2 g.
Acetone—500 cc.
Methanol—500 cc.

The thus obtained light-sensitive printing material was exposed to a 500 w. xenon lamp so that the exposed surface came to have an illuminance of 10,000 luxes and was then subjected to fixing in the same manner as in Example (2), whereby the exposure time could be shortened to 1/7–1/8 of the time required in the case of a conventional printing material.

Example (4)

In the same manner as in Example (2), a light-sensitive composition shown below was applied onto a photographic baryta paper.

Tribromomethylphenyl sulfone—10 g.
Diethanolaniline—30 g.
1,3-diphenyl-5-(p-methoxyphenyl)-pyrazoline (Sensitive IX)—5 g.
Thiourea—0.5 g.
Acetone—500 cc.
Methanol—500 cc.

When thiourea was added as a color tone modifier, the color tone of the resulting image changed from blue to dark blue upon exposure as in Example (2).

Example (5)

In the same manner as in Example (2), a light-sensitive emulsion of the composition shown below was applied onto a photographic baryta paper.

Carbon tetrabromide—10 g.
Indole—20 g.
1-Phenyl-3-diphenyl-5-(p-dimethylaminophenyl)-pyrazoline (Sensitive XII)—2 g.
Acetone—500 cc.
Methanol—500 cc.

The thus obtained light-sensitive printing material was exposed for 10 seconds to a 500 w. xenon lamp so that the exposed surface came to have an illuminance of 20,000 luxes to obtain an orange positive image with a white background. On the other hand, a control material containing no sensitizer required 30 seconds in obtaining a positive image of the same intensity by exposure under the same conditions as above.

EXAMPLE (6)

In the same manner as in Example (2), a light-sensitive emulsion of the composition shown below was applied onto a photographic baryta paper.

ω,ω,ω-Tribromoquinaldine—10 g.
Leuco malachite green—20 g.
1,3,5-triphenyl pyrazoline (Sensitizer VIII)—2 g.
Acetone—500 cc.
Methanol—500 cc.

The thus obtained light-sensitive printing material was exposed for 5 seconds to a 500 w. xenon lamp so that the exposed surface came to have an illuminance of 20,000 luxes to obtain a green positive image with a white background. On the other hand, a control material containing

no sensitizer required 10 seconds in obtaining a positive image of the same intensity by exposure under the same conditions as above.

Example (7)

In the same manner as in Example (2), a light-sensitive emulsion of the composition shown below was applied onto a photographic baryta paper.

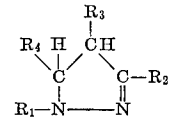
Hexabromodimethyl sulfone—0.1 g.
Ethyl violet—0.01 g.
1,3-Diphenyl-4-methyl-pyrazoline (Sensitizer VII)—0.02 g.
Ethanol—5.0 cc.
Acetone—5.0 cc.

The thus obtained light-sensitive printing material was exposed for 10 seconds to a 500 w. xenon lamp so that the exposed surface came to have an illuminance of 20,000 luxes to obtain a bleached colorless (white) negative image with a greenish blue background. On the other hand, a control material containing no sensitizer required 20 seconds in obtaining a negative image of the same extent by exposure under the same conditions as above.

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 imaging material comprising:
(a) a light-sensitive halogen-containing organic photoactivator capable of providing free radicals upon exposure to actinic light;
(b) a color-modifier capable of providing a visible color change by action of said free radicals; and
(c) between about 0.001 and 1.0 part per part of said photoactivator of a sensitizer of the general formula



wherein

R_1 is an aryl group;
R_2 is hydrogen, or an alkyl or aryl group;
R_3 is hydrogen, or an alkyl or aryl group; and
R_4 is hydrogen, or an aryl or oxygen-containing heterocyclic group.

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U.S. Cl. X.R.

117—34; 260—310