PATENT SPECIFICATION (11) 1 573 973

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(54) SENSITIVE PHOTOTHERMOGRAPHIC MATERIAL

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

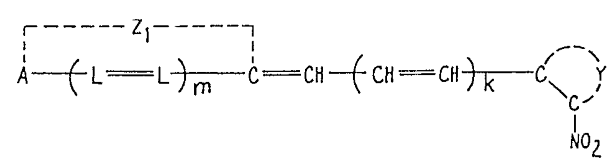
This invention relates to a sensitive photothermographic material.

An image may be obtained with a sensitive photothermographic material by imagewise exposure to radiation, commonly light, to form a latent image, and uniform heating to develop the latent image to a visible image. Such a material is convenient because it can provide an image without the use of processing solutions.

According to the present invention there is provided a sensitive photothermographic material which comprises a support coated with a composition containing an oxidation-reduction image-forming system comprising (a) a substantially radiation insensitive silver salt of an organic acid and (b) a non-radiation sensitive reducing agent therefor; (c) a photosensitive dye comprising an *o*-nitro substituted aryl nucleus joined by a methine linkage to a basic heterocyclic nucleus containing an electron-donating oxygen, sulphur or nitrogen atom, said atom and the nitro group being linked by a conjugated chain of carbon atoms; (d) a radiation-sensitive compound comprising a heterocyclic nucleus containing a nitrogen atom carrying an alkoxy or acyloxy group; and (e) a binder.

The *o*-nitro-substituted dye (c) is believed to form a reducing agent (photoreductant) upon exposure to light. The dye may conveniently be called an *o*-nitro substituted arylidene dye, the term "arylidene" referring to a group formed by an aryl group and a methine linkage (e.g., benzylidene or cinnamylidene). In a preferred dye the *o*-nitro-substituted aryl group is joined through a methine chain containing an odd number of methine groups to a basic nucleus of the kind present in cyanine dyes containing a 5- or 6-membered heterocyclic ring. This ring can have carbocyclic and/or heterocyclic rings fused thereto. The *o*-nitro-substituted aryl group may comprise a phenyl group or may comprise a nucleus formed of fused aromatic rings, such as a naphthyl group.

In a preferred embodiment of this invention, the photosensitive *o*-nitro-substituted dye has the formula:

I 

wherein:

(a) k represents 0 or 1;
(b) m represents 0 or 1;
(c) each L represents a methine (including a substituted methine) group (e.g., -CH= and -$C(CH_3)$=;
(d) A represents an electron donating moiety which is oxygen (-O-), sulphur (-S-), or $\underset{R_1}{\overset{}{\text{-N-}}}$;

(e) R_1 represents (1) an alkyl group preferably having from 1 to 18 carbon atoms and more preferably a lower alkyl group (i.e. an alkyl group having from 1 to 4 carbon atoms) which may be substituted. Examples of R_1 are e.g., methyl, ethyl, propyl, isopropyl, butyl, secondary-butyl, isobutyl, *tert*-butyl, pentyl, hexyl, octyl, decyl, dodecyl and octadecyl; a sulphoalkyl group, preferably sulpho lower alkyl (e.g., β-sulphoethyl, γ-sulphopropyl, γ-sulphobutyl or δ-sulphobutyl); a carboxyalkyl, preferably carboxy lower alkyl, group (e.g., β-carboxyethyl, γ-carboxypropyl or δ-carboxybutyl), a sulphatoalkyl preferably sulphato lower alkyl, group (e.g. δ-sulphatobutyl); an alkoxyalkyl, preferably lower alkoxy lower alkyl, group (e.g. β-methoxyethyl, γ-methoxypropyl or δ-propoxybutyl); an acyloxyalkyl, preferably acyloxy lower alkyl, group (e.g. acetyloxyethyl, propanoyloxyethyl, butanoyloxybutyl, benzoyloxyethyl or toloyloxypropyl); an alkoxycarbonylalkyl, preferably lower alkoxy carbonyl lower alkyl, group (e.g. β-methoxycarbonylethyl, δ-ethoxycarbonylbutyl or β-butoxycarbonylethyl); a dialkylaminoalkyl, preferably di-lower alkylamino lower alkyl, group (e.g. dimethylaminoethyl, diethylaminopropyl or diethylaminobutyl); a cycloaminoalkyl group, preferably cycloamino lower alkyl containing 4 to 6 atoms in the cycloamino moiety (e.g., pyrrolidinylethyl, morpholinopropyl, piperidinobutyl or pyrrolinylmethyl); (2) an alkenyl group (including a substituted alkenyl group), preferably a lower alkenyl containing 2 to 4 carbon atoms (e.g., ethylene, allyl, 1-propenyl-1-butenyl or 2-butenyl), or (3) an aryl group (including a substituted aryl) e.g., phenyl, naphthyl, tolyl, xylyl, halophenyl such as *p*-chlorophenyl or *p*-bromophenyl, alkoxyphenyl such as methoxyphenyl or 2,4-dichlorophenyl and an aralkyl group, preferably an aryl lower alkyl group (e.g. benzyl, β-phenethyl or ω-phenbutyl);

(f) Y represents the atoms necessary to complete an aryl (preferably phenyl or naphthyl) ring which is *ortho*-nitro-substituted, as shown in the formula, and preferably is also *para*-substituted with a nitro or other electron-withdrawing group such as

$$-\overset{\overset{\displaystyle O}{\|}}{C}OCH_3,$$

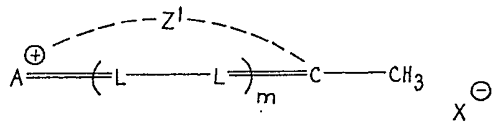
and which can have an electron-withdrawing group and which can have other substituents attached to it and other carbocyclic rings fused to it (e.g., 2-nitrophenyl, 2,4-dinitrophenyl, 2,6-dinitrophenyl, 2,4,6-trinitrophenyl, 2-nitronaphthyl, 2,4-dinitronaphthyl, 2-nitro-4-cyanophenyl, 2-nitro-4-ethoxycarbonylphenyl or 2-nitro-4-trifluoro-methylphenyl); and

(g) Z_1 represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes containing 5 or 6 atoms in the heterocyclic ring containing the moiety A which ring can contain a second hetero atom such as oxygen, nitrogen, selenium or sulphur. The heterocyclic nucleus preferably is selected from the group consisting of a thiazole nucleus including substituted and unsubstituted benzothiazole and naphthothiazole nuclei and like, (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 4-methylbenzothiazole, 4-methoxybenzothiazole, 4-ethoxybenzothiazole, 4-phenylbenzothiazole, 5-chlorobenzothiazole, 5-bromobenzothiazole, 5-methylbenzothiazole, 5-methoxybenzothiazole, 5-ethoxybenzothiazole, 5-phenylbenzothiazole, 6-chlorobenzothiazole, 6-bromobenzothiazole, 6-methylbenzothiazole, 6-methoxybenzothiazole, 6-ethoxybenzothiazole, 5-methoxynaphtha[2,3-d]thiazole, β-naphthothiazole, α-naphthothiazole, 5-nitrobenzothiazole, 6-nitrobenzothiazole or 5-chloro-6-nitrobenzothiazole); an oxazole nucleus including substituted and unsubstituted benzoxazole and naphthoxazole nuclei (e.g., oxazole, 4-phenyloxazole, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-bromobenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-phenylbenzoxazole, 5-methoxynaphthoxazole, 5-nitrobenzoxazole, 6-nitrobenzoxazole or 5-chloro-6-nitrobenzoxazole); a selenazole nucleus including substituted and unsubstituted benzoselenazole and naphthoselenazole nuclei (e.g., selenazole, 4-methylselenazole, 4-nitroselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 6-chlorobenzoselenazole, naphtho[2,1-d]selenazole, 5-nitrobenzoselenazole, 6-nitrobenzoselenazole, 5-chloro-6-nitrobenzoselenazole or nitro group-substituted naphthoselenazoles); a thiazoline nucleus, (e.g., thiazoline, 4-methylthiazoline, 4-nitrothiazoline or); a 2-pyridine nucleus, (e.g., 2-pyridine or 5-methyl-2-pyridine); a 4-pyridine nucleus, (e.g., 4-pyridine, 3-methyl-4-pyridine or a nitro group-substituted pyridine); a 3,3-dialkylindolenine nucleus (e.g., 3,3-dimethylindolenine, 3,3-diethyl-5 or 6-cyanoindolenine, 3,3-diethyl-5 or 6-nitroindolenine or 3,3-dimethyl-5 or 6-nitroindolenine); an imidazole nucleus, (e.g., imidazole, 1-alkylimidazole, benzimidazole or a 1,3-dialkyl, 1,3-diaryl or 1-alkyl-3-arylimidazole or benzimidazole, such as 5-chloro-1,3-dialkylbenzimidazoles, 5-chloro-1,3-diarylbenzimidazoles, 5,6-dichloro-1,3-

diarylbenzimidazoles, 5-methoxy-1,3-dialkylbenzimidazoles, 5-methoxy-1,3-diarylbenzimidazoles, 5-cyano-1,3-dialkylbenzimidazoles, 5-cyano-1,3-diarylbenzimidazoles, 1,3-dialkylnaphth[1,2-d]imidazole or 1,3-diarylnaphth[2,1-d]imidazole); a quinoline nucleus, (e.g., quinoline, 6-methylquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-chloroquinoline, 4-methoxyquinoline, 4-methylquinoline, 8-methoxyquinoline, β-methylquinoline, 4-chloroquinoline or 6-nitroquinoline); an imidazo[4,5-b]quinoxaline nucleus (as described in Brooker and Van Lare, U.S. Patent 3,431,111), (e.g., imidazo[4,5-b]quinoxaline, a 1,3-dialkylimidazo[4,5-b]-quinoxaline such as 1,3-diethylimidazo[4,5-b]quinoxaline or 6-chloro-1,3-diethylimidazo[4,5-b]quinoxaline, a 1,3-dialkenylimidazo[4,5-b]quinoxaline such as 1,3-diallylimidazo[4,5-b]quinoxaline or 6-chloro-1,3-diallylimidazo[4,5-b]quinoxaline; a 1,3-diarylimidazo[4,5-b]quinoxaline such as 1,3-diphenylimidazo[4,5-b]quinoxaline or 6-chloro-1,3-diphenylimidazo[4,5-b]quinoxaline); a 3H-pyrrolo[2,3-b]pyridine nucleus, e.g. a 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine such as 3,3-dimethyl-3H-pyrrolo[2,3-b]pyridine, 3,3-diethyl-3H-pyrrolo[2,3-b]pyridine or 1,3,3-trialkyl-3H-pyrrolo[2,3-b]; a pyridine such as 1,3,3-triethyl-3H-pyrrolo[2,3-b]pyridine); and a thiazolo[4,5-b]quinoline nucleus; a pyrylium (including benzopyrylium, thiapyrylium and benzothiapyrylium) nucleus; and a dithiolinium nucleus. In the most preferred embodiment Z_1 represents the atoms necessary to form a pyridine or a quinoline nucleus.

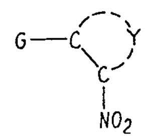
The above dyes, wherein k represents 0, preferably are prepared by reacting a heterocyclic salt of the formula:

II.



with a nitro-substituted compound having the formula:

III.



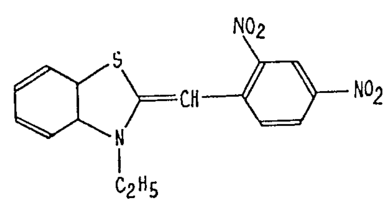
In the above formulae II and III, m, A, Z_1, L, and Y are as defined above, G represents a halogen atom such as fluorine, chlorine or bromine, and $X^{\ominus}$ represents an acid anion (e.g., halide such as chloride, bromide, or iodide, *p*-toluenesulphonate, thiocyanate, sulphamate, perchlorate fluoroborate, methylsulphonate, ethylsulphonate, fluorosulphonate or 2,4-dinitrobenzenesulphonate).

The preparation of dyes according to the description above is described in Belgian Patent 788,279 and U.K. Patent 1,399,751.

Examples of useful nitrobenzylidene dyes which can be used with the compounds (d) are the Dyes 1 to 8 specified below:

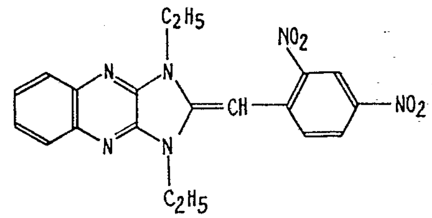
Dye 1

2-(2,4-Dinitrobenzylidene)-3-ethylbenzothiazoline



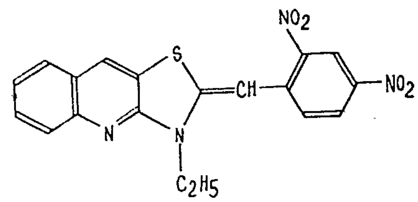
Dye 2

2-(2,4-Dinitrobenzylidene)-1,3-diethyl-1,2-dihydroimidazo[4,5-b]quinoxaline



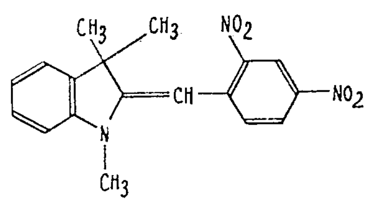
Dye 3

2-(2,4-Dinitrobenzylidene)-3-ethyl-2,3-dihydrothiazolo[4,5-b]quinoline



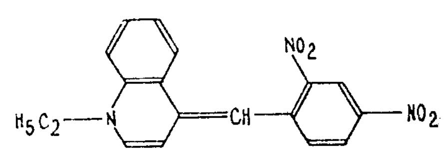
Dye 4

2-(2,4-Dinitrobenzylidene)-1,3,3-trimethylindoline



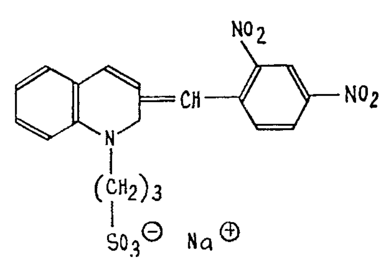
Dye 5

4-(2,4-Dinitrobenzylidene)-1-ethyl-1,4-dihydroquinoline



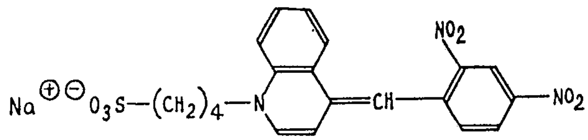
Dye 6

2-(2,4-Dinitrobenzylidene)-1,2-dihydro-1-(3-sulphopropyl)quinoline, sodium salt



Dye 7

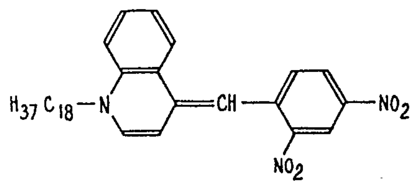
4-(2,4-Dinitrobenzylidene)-1,2-dihydro-1-(4-sulphobutyl)quinoline, sodium salt



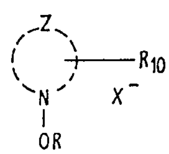
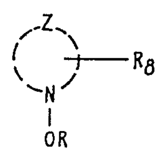
and

Dye 8

1,4-Dihydro-4-(2,4-dinitrobenzylidene)-1-octadecylquinoline



The photosensitive compound (d) containing a heterocyclic nitrogen atom which is substituted by an alkoxy or acyloxy group typically may have one of the general formulae:

IIa  or 

wherein:

R_{10} is any of the following:

(a) a methine linkage terminated by a heterocyclic nucleus of the type contained in cyanine dyes, e.g. those set forth in Mees and James, "The Theory of the Photographic Process," Macmillan, 3rd ed., pp. 198-232; the methine linkage can be substituted or unsubstituted, e.g., -CH=, -C(CH_3)=, -C(C_6H_5)=, -CH=CH- or -CH=CH-CH=;

(b) an alkyl radical preferably containing one to eight carbon atoms, which may be substituted;

(c) an aryl or substituted aryl radical such as a phenyl, naphthyl radical or tolyl radical;

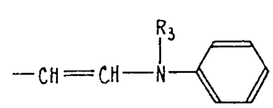
(d) hydrogen;

(e) an acyl radical having the formula

$$- \overset{O}{\overset{\|}{\mathrm{C}}} - R_9$$

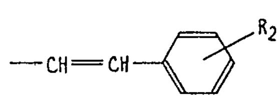
wherein R_9 is hydrogen or an alkyl group preferably having one to eight carbon atoms;

(f) an anilinovinyl radical such as a radical having the formula



wherein R_3 is hydrogen, acyl or alkyl; or

(g) a styryl radical including substituted styryl radicals, e.g.,



wherein R_2 is hydrogen, alkyl, aryl or amino including dialkylamino such as dimethylamino;

R_8 is either:

(a) a methine linkage terminated by a heterocyclic nucleus of the type contained in merocyanine dyes, e.g., those set forth in Mees and James (cited above); the methine linkage can be substituted or unsubstituted; or

(b) an allylidene radical including a substituted allylidene radical such as a cyanoallylidene radical, an alkylcarboxy-allylidene radical or an alkylsulphonylallylidene radical;

R is either:

(a) an alkyl radical preferably having one to eight carbon atoms such as methyl, propyl, ethyl or butyl, which may be substituted, for instance sulphoalkyl (e.g. $-(CH_2)_3\ SO_3$-), aralkyl (e.g., benzyl or pyridinatooxyalkyl salt such as $-(CH_2)_3$-O-Q wherein Q is substituted or unsubstituted pyridinium salt; or

(b) an acyl radical, e.g.,

$$-\overset{\displaystyle O}{\overset{\|}{C}}-R_4$$

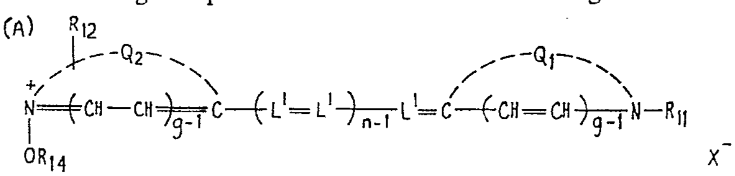
wherein R_4 is an alkyl radical preferably having one to eight carbon atoms, or an aryl radical, e.g. methyl, ethyl, propyl, butyl, phenyl or naphthyl.

Z represents the atoms necessary to complete a 5- or 6-membered ring containing heterocyclic nucleus which may be substituted and may contain at least one additional hetero atom such as an oxygen, sulphur, selenium or nitrogen atom. For example Z may complete a pyridine or a quinoline nucleus; and

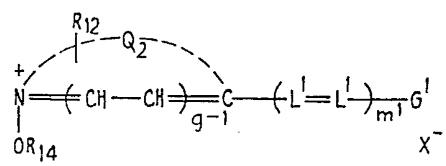
X^- represents an acid anion, e.g., chloride, bromide, iodide, perchlorate, sulphamate, thiocyanate, p-toluenesulphonate, methylsulphate or tetrafluoroborate.

The preferred sensitizing compounds have one of the following structures:

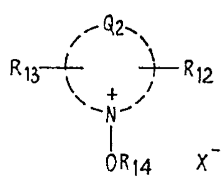
(A)



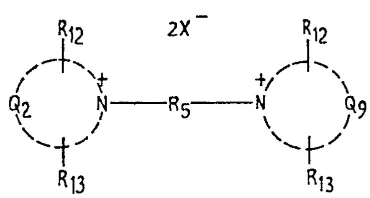
(B)



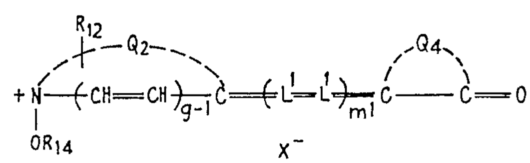
(C)



(D)

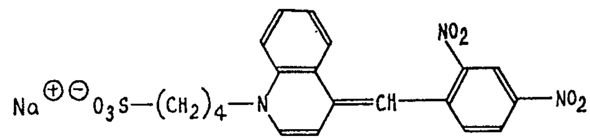


(E)



Dye 7

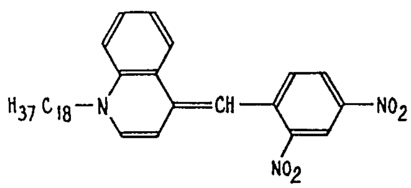
4-(2,4-Dinitrobenzylidene)-1,2-dihydro-1-(4-sulphobutyl)quinoline, sodium salt



and

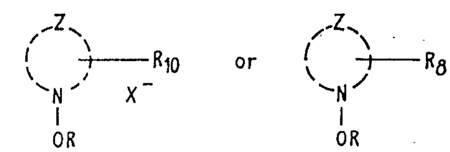
Dye 8

1,4-Dihydro-4-(2,4-dinitrobenzylidene)-1-octadecylquinoline



The photosensitive compound (d) containing a heterocyclic nitrogen atom which is substituted by an alkoxy or acyloxy group typically may have one of the general formulae:

IIa



wherein:

R_{10} is any of the following:

(a) a methine linkage terminated by a heterocyclic nucleus of the type contained in cyanine dyes, e.g. those set forth in Mees and James, "The Theory of the Photographic Process," Macmillan, 3rd ed., pp. 198-232; the methine linkage can be substituted or unsubstituted, e.g., -CH=, $-C(CH_3)=$, $-C(C_6H_5)=$, -CH=CH- or -CH=CH-CH=;

(b) an alkyl radical preferably containing one to eight carbon atoms, which may be substituted;

(c) an aryl or substituted aryl radical such as a phenyl, naphthyl radical or tolyl radical;

(d) hydrogen;

(e) an acyl radical having the formula

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wherein R_9 is hydrogen or an alkyl group preferably having one to eight carbon atoms;

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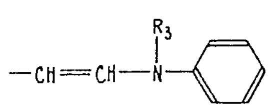
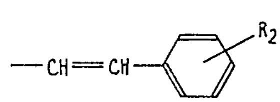


wherein R_3 is hydrogen, acyl or alkyl; or

(g) a styryl radical including substituted styryl radicals, e.g.,



wherein R_2 is hydrogen, alkyl, aryl or amino including dialkylamino such as dimethylamino;

R_8 is either:

(a) a methine linkage terminated by a heterocyclic nucleus of the type contained in merocyanine dyes, e.g., those set forth in Mees and James (cited above); the methine linkage can be substituted or unsubstituted; or

(b) an allylidene radical including a substituted allylidene radical such as a cyanoallylidene radical, an alkylcarboxy-allylidene radical or an alkylsulphonylallylidene radical;

R is either:

(a) an alkyl radical preferably having one to eight carbon atoms such as methyl, propyl, ethyl or butyl, which may be substituted, for instance sulphoalkyl (e.g. $-(CH_2)_3\ SO_3-$), aralkyl (e.g., benzyl or pyridinatooxyalkyl salt such as $-(CH_2)_3-O-Q$ wherein Q is substituted or unsubstituted pyridinium salt; or

(b) an acyl radical, e.g.,

$$-\overset{\displaystyle O}{\overset{\|}{C}}-R_4$$

wherein R_4 is an alkyl radical preferably having one to eight carbon atoms, or an aryl radical, e.g. methyl, ethyl, propyl, butyl, phenyl or naphthyl.

Z represents the atoms necessary to complete a 5- or 6-membered ring containing heterocyclic nucleus which may be substituted and may contain at least one additional hetero atom such as an oxygen, sulphur, selenium or nitrogen atom. For example Z may complete a pyridine or a quinoline nucleus; and

X^- represents an acid anion, e.g., chloride, bromide, iodide, perchlorate, sulphamate, thiocyanate, p-toluenesulphonate, methylsulphate or tetrafluoroborate.

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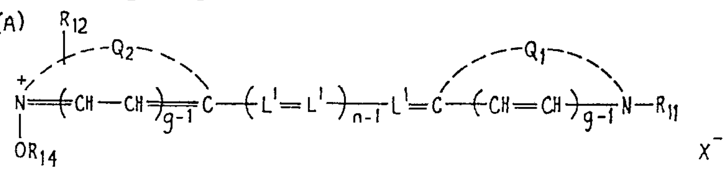
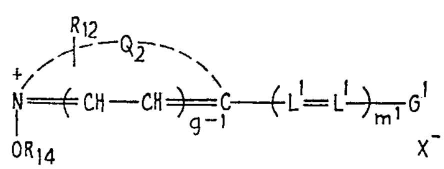
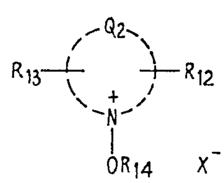
(A)



(B)



(C)



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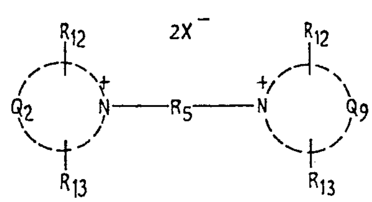

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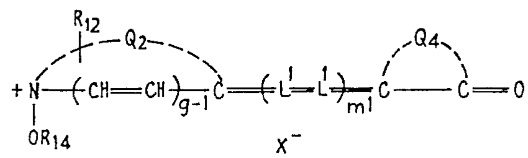
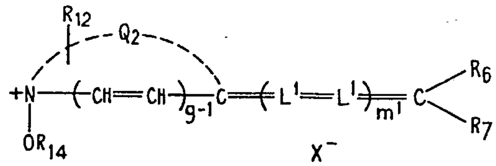


or

(F)



wherein Q_1, Q_2 and Q_9 each represent the nonmetallic atoms necessary to complete a sensitizing or desensitizing nucleus containing five or six atoms in the heterocyclic ring, which nucleus can contain at least one additional hetero atom such as oxygen, sulphur, selenium or nitrogen, i.e., a nucleus of the type used in the production of cyanine dyes, such as the following representative nuclei: a thiazole nucleus e.g., thiazole 4-methylthiazole, 3-ethylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 4- or 5-nitrobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 6-nitrobenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-chloro-6-nitrobenzothiazole, 4-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, a tetrahydrobenzothiazole nucleus, 5,6-dimethoxybenzothiazole, 5,6-methylenedioxybenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, α-naphthothiazole, β-naphthothiazole, β,β-naphthothiazole, 5-methoxy-β,β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole, 7-methoxy-α-naphthothiazole, 4″-methoxythianaptheno-7′,6′,4,5-thiazole or a nitro group substituted naphthothiazole; an oxazole nucleus, e.g., 4-methyloxazole, 4-nitro-oxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 5- or 6-nitrobenzoxazole, 5-chloro-6-nitrobenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, α-naphthoxazole, β-naphthoxazole or a nitro group substituted naphthoxazole; a selenazole nucleus, e.g., 4-methylselenazole. 4-nitroselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, 5- or 6-nitrobenzoselenazole, 5-chloro-6-nitrobenzoselenazole, tetrahydrobenzoselenazole, α-naphthoselenazole, β-naphthoselenazole, or a nitro group substituted naphthoselenazole; a thiazoline nucleus, e.g., thiazoline or 4-methylthiazoline; a pyridine nucleus, e.g., 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine or a nitro group substituted pyridine; a quinoline nucleus, e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 6-nitro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 6-nitro-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, 1-isoquinoline, 6-nitro-1-isoquinoline, 3,4-dihydro-1-isoquinoline or 3-isoquinoline; a 3,3-dialkylindolenine nucleus, preferably having a nitro or cyano substituent, e.g., 3,3-dimethyl-5- or 6-nitroindolenine or 3,3-dimethyl-5- or 6-cyano-indolenine; an imidazole nucleus, e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, benzimidazole, 1-alkylbenzimidazole, 1-alkyl-5-nitrobenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-alkyl-α-naphthimidazole, 1-aryl-β-naphthimidazole or 1-alkyl-5-methoxy-α-naphthimidazole; an imidazo[4,5-b]quinoxaline nucleus, e.g. a 1-alkylimidazo[4,5-b]quinoxaline such as 1-ethylimidazo[4,5-b]quinoxaline or 6-chloro-1-ethylimidazo[4,5-b]-quinoxaline; 1-alkenylimidazo[4,5-b]quinoxaline, such as 1-allylimidazo[4,5-b]quinoxaline, 6-chloro-1-allylimidazo[4,5-b]quinoxaline; a 1-arylimidazo[4,5-b]quinoxaline, such as 1-phenylimidazo[4,5-b]quinoxaline or 6-chloro-1-phenylimidazo[4,5-b]quinoxaline; a 3,3-dimethyl-3H-pyrrolo-[2,3-b]pyridine nucleus, e.g., 3,3-dimethyl-3H-pyrrolo[2,3-b]pyridine or 3,3-diethyl-3H-pyrrolo[2,3-b]pyridine; a thiazolo[4,5-b]quinoline nucleus; R_{11} represents an alkyl (preferably a lower alkyl containing from one to four carbon atoms), e.g. methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl or dodecyl, a substituted alkyl group (preferably a substituted lower alkyl containing from one to four carbon atoms), such as a hydroxyalkyl group, e.g., β-hydroxyethyl or ω-hydroxybutyl, an alkoxyalkyl group, e.g., β-methoxyethyl or ω-butoxybutyl, a carboxyalkyl group, e.g. β-carboxyethyl or ω-carboxybutyl, an alkoxy group, e.g., methoxy or ethoxy, a sulphoalkyl group, e.g., β-sulphoethyl or ω-sulphobutyl, a sulphatoalkyl group, e.g., β-sulphoatoethyl or ω-sulphatobutyl, an acyloxyalkyl group, e.g., β-acetoxyethyl, γ-acetoxypropyl or ω-butyryloxybutyl, an alkoxycarbonyl-alkyl group, e.g., β-methoxycarbonylethyl or ω-ethoxycarbonylbutyl, or an aralkyl group, e.g., benzyl or phenethyl; an alkenyl group, e.g., allyl, 1-propenyl or 2-butenyl, or an aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl or chlorophenyl; Q_4 represents the nonmetallic atoms required to complete a 5 to 6 membered heterocyclic nucleus, typically containing a hetero atom selected from nitrogen, sulphur, selenium, and oxygen, such as a 2-pyrazolin-5-one nucleus (e.g., 3-methyl-1-phenyl)-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one or 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one); an isoxazoline nucleus (e.g., 3-phenyl-5(4H)-isoxazoline, 3-methyl-5-(4H)-isoxazolone or 3-methyl-5-(4H)-isoxazolone); an oxindole nucleus (e.g. a 1-alkyl-2,3-dihydro-2-oxindole), a 2,4,6-triketohexahydropyrimidine nucleus (e.g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-propyl or 1-heptyl) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl or 1,3-di-(β-methoxyethyl) or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl) or 1,3-di(p-ethoxycarbonylphenyl) or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl or 1-*p*-ethoxycarbonylphenyl) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl or 1-n-heptyl-3-phenyl) derivatives), a rhodanine nucleus (i.e., 2-thio-2,4-thiazolidinedione series), such as rhodanine, a 3-alkylrhodanine (e.g., 3-ethylrhodanine or 3-allylrhodanine), a 3-carboxyalkylrhodanine (e.g., 3-(2-carboxyethylrhodanine or 3-(4-carboxybutylrhodanine), a 3-sulphoalkyl rhodanines (e.g., 3-(2-sulphoethyl)rhodanine, 3-(3-sulphopropyl)rhodanine or 3-(4-sulphobutyl)rhodanine), or a 3-arylrhodanine (e.g., 3-phenylrhodanine), a 2(3H)-imidazo[1,2-a]pyridone nucleus, a 2-furanone nucleus (e.g., 3-cyano-4-phenyl-2(5H)-furanone), a thiophen-3-one-1,1-dioxide nucleus (e.g., benzo-1[b]thiophen-3(2H)-one-1,1-dioxide); a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus (e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine), a 2-thio-2,4-oxazolidinedione nucleus (i.e., those of the 2-thio-2,4(3H, 5H)-oxazoledione series) (e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-oethyl)-2-thio-2,4-oxazolidinedione, 3-(4-sulphobutyl)-2-thio-2,4-oxazolidinedione or 3-(3-carboxypropyl)-2-thio-2,4-oxazolidinedione); a thianaphthenone nucleus (e.g., 2-(2H)-thianaphthenone); a 2-thio-2,5-thiazolidinedione nucleus (i.e., the 2-thio-2,5(3H, 4H)-thiazoledione series) (e.g., 3-ethyl-2-thio-2,5-thiazolidinedione); a 2,4-thiazolidinedione nucleus (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione or 3-α-naphthyl-2,4-thiazolidinedione); a thiazolidinone nucleus (e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone or 3-α-naphthyl-4-thiazolidinone); a 2-thiazolin-4-one (e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkylphenylamino-2-thiazolin-4-one or 2-diphenylamino-2-thiazoline-4-one); a 2-imino-4-oxyazolidinone (i.e. pseudohydantoin) nucleus, a 2,4-imidazolidinedione (hydantoin) series (e.g., a, 4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3-α-naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2,4-imidazolidinedione, 1-ethyl-2-α-naphthyl-2,4-imidazolidinedione or 1,3-diphenyl-2,4-imidazolidinedione); a 2-thio-2,4-imidazolidinedione (i.e. 2-thiohydantoin)nucleus (e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-imidazolidinedione, 3-(4-sulphobutyl)-2-thio-2,4-imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolidinedione, 3-phenyl-2-thio-2,4-imidazolidinedione, 3-α-naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-α-naphthyl-2-thio-2,4-imidazolidinedione or 1,3-diphenyl-2-thio-2,4-imidazolidinedione); a 2-imidazolin-5-one nucleus (e.g., 2-propylmercapto-2-imidazolin-5-one);

n is 1, 2, 3 or 4;

m^1 is 1, 2 or 3;

g is 1 or 2;

R_6 and R_7 each represent a cyano radical, an ester radical such as ethoxycarbonyl or methoxycarbonyl, or an alkylsulphonyl radical such as ethylsulphonyl or methylsulphonyl;

L^1 represents a methine linkage having the formula

$$\begin{array}{c} -\mathrm{C}= \\ | \\ \mathrm{T} \end{array}$$

wherein T is hydrogen, lower alkyl of one to four carbon atoms or aryl such as phenyl, e.g., -CH=, $-C(CH_3)=$, $-C(C_6H_5)=$;

R_{12} and R_{13} each represent a hydrogen atom, an alkyl group (preferably a lower alkyl containing from one to four carbon atoms), e.g., methyl, ethyl, propyl, ispropyl, butyl, decyl or dodecyl, or an aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl or nitrophenyl;

X represents an acid anion, e.g., chloride, bromide, iodide, perchlorate, tetrafluoroborate, sulphamate, thiocyanate, p-toluene or methyl sulphate;

G^1 represents an anilino radical or an aryl radical, e.g., phenyl, naphthyl, dialkylaminophenyl, tolyl, chlorophenyl, nitrophenyl or anilinovinyl;

R_5 is an alkyleneoxy radical having one to eight carbon atoms in the alkylene chain including an alkylenedioxy radical and an arylenebisalkoxy radical e.g., ethyleneoxy, trimethyleneoxy, tetramethyleneoxy, propylideneoxy, ethylenedioxy or phenylenebisethoxy;

R_{14} represents either (1) an alkyl radical including a substituted alkyl (preferably a lower alkyl having one to four carbon atoms); e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, aralkyl such as benzyl, oalkyl such as β-sulphoethyl, ω-sulphobutyl or γ-sulphopropyl; or (2) an acyl radical, e.g.,

$$-\overset{\overset{\displaystyle O}{\|}}{C}-R_4$$

wherein R_4 is an alkyl, including a substituted alkyl, or an aryl radical such as methyl, phenyl, naphthyl, propyl or benzyl.

In the above formulae Q_2 preferably completes a pyridine or a quinoline nucleus.

Typical sensitizing compounds included are the following:

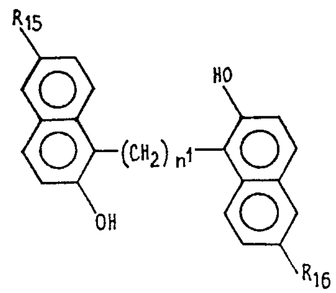
1. 3-ethyl-1′-methoxyoxa-2′-pyridocarbocyanine perchlorate
2. 1′-ethoxy-3-ethyloxa-2′-pyridocarbocyanine tetrafluoroborate
3. 3′-ethyl-1-methoxy-2-pyridothiacyanine iodide
4. 1-ethoxy-3′-ethyl-2-pyridothiacyanine tetrafluoroborate
5. 1-benzyloxy-3′-ethyl-2-pyridothiacyanine iodide
6. 3′-ethyl-1-methoxy-2-pyridothiacarbocyanine iodide
7. 1-ethoxy-3′-ethyl-2-pyridothiacarbocyanine tetrafluoroborate
8. anhydro-3′-ethyl-1-(3-sulfopropoxy)-2-pyridothiacarbocyanine hydroxide
9. 1-benzyloxy-3′-ethyl-2-pyridothiacarbocyanine perchlorate
10. 3′-ethyl-1-methoxy-2-pyridothiacarbocyanine perchlorate
11. 1′-methoxy-3,3-trimethylindo-2′-pyridocarbocyanine picrate
12. 3′-ethyl-1-methoxy-4′,5′-benzo-2-pyridothiacarbocyanine perchlorate
13. 1-ethoxy-3′-ethyl-4′,5′-benzo-2-pyridothiacarbocyanine tetrafluoroborate
14. 1′-ethoxy-3-ethyloxa-2′-carbocyanine tetrafluoroborate
15. 1′-ethoxy-3-ethylthia-2′-cyanine tetrafluoroborate
16. 1′-ethoxy-3-ethylthia-2′-carbocyanine tetrafluoroborate
17. 1′-ethoxy-3-ethylthia-2′-dicarbocyanine tetrafluoroborate
18. 1-methoxy-3′-methyl-2-pyridothiazolinecarbocyanine perchlorate
19. 3′-ethyl-1-methoxy-4-pyridothiacyanine perchlorate
20. 3′-ethyl-1-methoxy-4-pyridothiacarbocyanine perchlorate
21. 1′-ethoxy-3-ethyl-4,5-benzothia-2′-carbocyanine tetrafluoroborate
22. 2-β-anilinovinyl-1-methoxypyridinium p-toluenesulfonate
23. 1-ethyl-1′-methoxy-4,5-benzothia-4′-carbocyanine perchlorate
24. 1-methoxy-2-methylpyridinium p-toluenesulfonate
25. 1-methoxy-4-methylpyridinium p-toluenesulfonate
26. anhydro-2-methyl-1-(3-sulfopropoxy)pyridinium hydroxide
27. 1-ethoxy-2-methylpyridinium tetrafluoroborate
28. 1-benzyloxy-2-methylpyridinium bromide
29. 1-ethoxy-2-methylquinolinium tetrafluoroborate
30. 1,1′-ethylenedioxybispyridinium dibromide
31. 1,1′-trimethylenedioxybispyridinium dibromide
32. 1,1′-tetramethylenedioxybis(2-methylpyridinium)dibromide
33. 1,1′-tetramethylenedioxybis(4-methylpyridinium)dibromide
34. 1,1′-tetramethylenedioxybispyridinium dibromide
35. 1,1′-pentamethylenedioxybispyridinium dibromide
36. 1-acetoxy-2-(4-dimethylaminostyryl)pyridinium perchlorate
37. 1-benzoyloxy-2-(4-dimethylaminostyryl)pyridinium perchlorate
38. 1,3-diethyl-5-[(1-methoxy-2(1H)-pyridylidene)ethylidene]-2-thiobarbituric acid
39. 3-ethyl-5-[(1-methoxy-2(1H)-pyridylidene)ethylidene]rhodanine
40. 1,3-diethyl-5-[(1-methoxy-2(1H)-pyridylidene)ethylidene]barbituric acid
41. 2-(3,3-dicyanoallylidene)-1-methoxy-1,2-dihydropyridine
42. 2-[(1-methoxy-2(1H)-pyridylidene)-ethylidene]benzo[b]-thiophen-3(2H)-one-1,1-dioxide
43. 3-cyano-5-[(1-methoxy-2(1H)-pyridylidene methylidene]-4-phenyl-2(5H)-furanone.

The preparation of these compounds according to the description given above is described in U.K. Patent 1,281,565.

In a material of the invention each radiation sensitive dye is preferably present at a concentration in the range of from 10^{-5} to 10^{-1} mole per mole of silver in the reducible silver salt, a concentration in the range from 10^{-4} to 10^{-2} mole per mole of silver being particularly preferred.

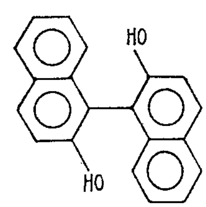
The photothermographic materials and compositions according to the invention comprise an oxidation-reduction image-forming system which contains a reducible silver salt of an organic acid, which salt is resistant to darkening upon illumination. An especially useful class of silver salts of organic acids is constituted by the water-insoluble silver salts of long-chain fatty acids having at least 10 carbon atoms which are stable to light such as silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate and silver palmitate. Useful silver salts which are not salts of long-chain fatty acids, include such salts as silver benzoate, silver benzotriazole, silver terephthalate and silver phthalate.

A range of organic non-radiation sensitive reducing agents can be employed in the practice of the invention to provide a desired developed image. Preferred are bis-β-naphthols of the formula:



wherein R_{15} and/or R_{16} is hydrogen, alkyl with 1 to 3 carbon atoms, alkoxy (e.g. alkoxy containing 1 to 2 carbon atoms), halogen, nitro, amino, or a diazonium halide salt and n' is 0 or 1.

An especially suitable bis-β-naphthol is 1,1'-bi-2-naphthol of the formula:



Other suitable bis-β-naphthols are:

6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl
6,6'-dinitro-2,2'-dihydroxy-1,1'-dinaphthyl
bis-(2-hydroxy-1-naphthyl)methane.

The reducing agent (or reducing agent mixture) is preferably used at a concentration of from 0.1 to 0.75 mole per mole of silver in the reducible silver salt.

Other non-light sensitive reducing agents can be used in lieu of or in conjunction with the above bis-naphthol reducing agents including polyhydroxybenzenes such as hydroquinone developing agents, e.g. hydroquinone itself, alkyl-substituted hydroquinones such as tertiary butylhydroquinone, methylhydroquinone, 2,5-dimethylhydroquinone and 2,6-dimethylhydroquinone; halo-substituted hydroquinones such as chlorohydroquinone and dichlorohydroquinone; and alkoxy-substituted hydroquinones such as methoxyhydroquinone and ethoxyhydroquinone; catechols and pyrogallol; methoxynaphthalene, phenylenediamine developing agents; methylgallate; aminophenol developing agents, such as 2,4-diaminophenols and methylaminophenols; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals and ascorbic acid derivatives such as those described in

U.S. Patent 3,337,342; hydroxylamine developing agents such as N,N'-di(2-ethoxyethyl)hydroxylamine; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidones and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone (see for instance British Patent 930,572); hydroxytetronic acid, and hydroxytetronimide developing agents; reductone developing agents such as anhydrodihydropyrrolidino hexose reductone; and sulphonamidophenol reducing agents such as are described in U.S. Patent 3,801,321.

The photothermographic material or composition can contain various colloids alone or in combination as binders. The preferred binders are hydrophobic but hydrophilic binders can also be employed. Suitable binders include both naturally-occurring substances, and their derivatives, such as gelatin, gelatin derivatives, cellulose derivatives and polysaccharides, such as dextran and gum arabic, and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinyl pyrrolidone) and acrylamide polymers. Other synthetic polymeric compounds which can be employed include dispersed vinyl compounds, for instance in latex form, particularly those which increase dimensional stability of photographic materials. Suitable synthetic polymers are those described in U.S. Patents 3,142,568, 3,193,386, 3,062,674, 3,220,844, 3,287,289, and 3,411,911. Effective polymers include water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, and those which have crosslinking sites which facilitate hardening or curing as well as those having recurring sulfobetaine units as described in Canadian Patent 774,054. Preferred high molecular weight materials and resins include poly(vinyl butyral), cellulose acetate butyrate, polymethyl methacrylate, poly(vinyl pyrrolidone), ethyl cellulose, polystyrene, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid, polyvinyl alcohol, and high molecular weight ethylene oxide polymers.

It is often desirable to employ a so-called activator toning agent, also known as an accelerator-toning agent, in the photothermographic materials according to the invention to obtain a desired image. The activator toning agent is typically useful at a concentration of from 0.10 to 1.1 moles per mole of the reducible heavy metal salt. A typical suitable activator toning agent is a heterocyclic activator toning agent containing at least one nitrogen atom as described, for example, in Belgian Patent No. 766,590 and U.S. Patent 3,846,136. Typical activator toning agents include cyclic imides, such as phthalimide, N-hydroxyphthalimide, N-hydroxy-1,8-naphthalimide, N-potassium phthalimide, N-mercury phthalimide, succinimide and/or hydroxysuccinimide. Other activator toning agents which can be employed include phthalazinone and 2-acetylphthalazinone.

An especially useful photothermographic material according to the invention comprises a support having thereon an oxidation-reduction image-forming combination comprising (1) 1,1'-bi-2-naphthol and (2) silver behenate, (a) a poly(viny butyral) binder, (b) phthalimide and (c) a combination of 4-(2,4-dinitrobenzylidene)-1-ethyl-1,4-dihydroquinoline and 2-β-anilinovinyl-1-methoxypyridinium, p-toluene sulphonate.

Photothermographic materials according to the invention can contain hardeners, antistatic layers, development modifiers that function as speed-increasing compounds, plasticizers and lubricants, coating aids, brighteners, spectral sensitizing dyes, absorbing and filter dyes, also as described in the *Product Licensing Index*, Volume 92, December 1971, publication 9232, pp. 107-110.

A photothermographic composition and any other composition used in making a sensitive material according to the invention can be coated on the chosen support by various procedures including dip coating, air knife coating, curtain coating and extrusion coating using hoppers such as described in U.S. Patent 2,681,294 of Beguin. If desired, two or more layers can be coated simultaneously, for instance as described in U.S. Patent No. 2,761,791 and British Patent No. 837,095.

After exposure of a photothermographic material according to the invention, typically to visible light, the resulting latent image can be developed to a negative image merely by overall heating the material to a moderately elevated temperature in the approximate range 80 to 250°C, preferably 110 to 165°C, for a time of from 0.5 second to 60 seconds. By using a higher temperature within the described range, more rapid processing may be achieved. Any suitable means can be used for heating such as a hot plate, iron or roller.

If desired, a photothermographic material of this invention can be simultaneously imagewise exposed and heat processed to give a negative image. The photothermographic materials of this invention are especially useful because they allow positive as well as negative images to be obtained. To form a direct positive image, the material is exposed imagewise to ultraviolet light, is then exposed overall to radiation (possibly visible light from a tungsten lamp) absorbed by the nitrobenzylidene dye, and is then heated to a temperature within the approximate range 80 to 250°C for a time of from about 0.5 second to about 60 seconds. The necessary time of exposure to a tungsten lamp generally is from 5 to 15 seconds.

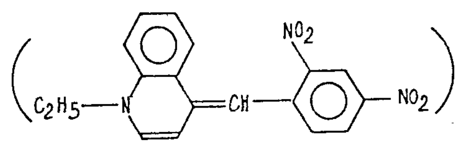
Example 1 - Dispersion A

A silver behenate dispersion was prepared by ball-milling the following composition for about 72 hours:

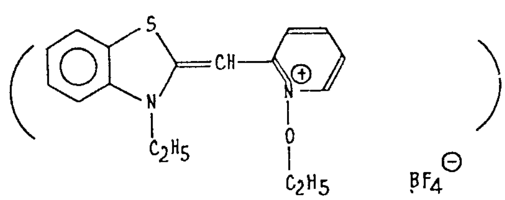
Silver behenate	168 grams
Poly(vinyl butyral)	120 grams
Acetone-toluene (1:1 parts by volume)	1600 mls

A photothermographic material was prepared by coating the following composition on a photographic paper support at a wet thickness of 0.1 mm.

Dispersion A	11.4 ml
1,1'-bi-2-naphthol (6.3% by weight in acetone)	4.3 ml
phthalimide (5.0% by weight in acetone)	4.3 ml
4-(2,4-dinitrobenzylidene)-1-ethyl-1,4-dihydroquinoline (1 milligram per millilitre of acetone)	5.0 ml



1'-ethoxy-3-ethylthia-2'-pyridocyanine tetrafluoroborate (1 milligram per millilitre of acetone)	5.0 ml



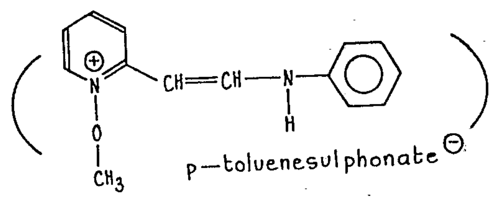
The photothermographic material was imagewise exposed for 15 seconds to ultraviolet light and then overall exposed to a filtered (KODAK 'Wratten' 25) No. 2 photoflood lamp for 10 seconds ('Kodak' and 'Wratten' are trade marks). The exposed sample was overall heat processed for 20 seconds on a curved hot block at a temperature of 122°C. A positive image resulted.

Example 2

A photothermographic material was prepared by coating the following composition on a photographic paper support at a wet thickness of 0.1 mm.

Dispersion A of Example 1	11.4 ml
1,1'-bi-2-naphthol (6.3% by weight in acetone)	4.3 ml
phthalimide (5.0% by weight in acetone)	4.3 ml
4-(2,4-dinitrobenzylidene)-1-ethyl-1,4-dihydroquinoline (1 milligram per millilitre of acetone)	5.0 ml

2-β-anilinovinyl-1-methoxypyridinium p-toluenesulphonate (1 milligram per millilitre of acetone)	5.0 ml



The photothermographic material was imagewise exposed for 15 seconds to ultraviolet light and then overall exposed to a filtered (KODAK 'Wratten' 25) number 2 photoflood lamp for 10 seconds. The exposed sample was overall heat processed for 20 seconds on a curved hot block at a temperature of 122°C. A positive image resulted.

Example 3

A photothermographic material was prepared by coating the following composition on a photographic paper support at a wet thickness of 0.1 mm:

silver behenate Dispersion A of Example 1	8.7 ml
1,1'-bi-2-naphthol (6.3% by weight in acetone)	3.3 ml
phthalimide (5.0% by weight in acetone)	3.3 ml
4-(2,4-dinitrobenzylidene)-1-ethyl-1,4-dihydroquinoline (1 milligram per millilitre of acetone)	4.7 ml
2-β-anilinovinyl-1-methoxypyridinium p-toluenesulphonate (1 milligram per millilitre of acetone)	10.0 ml

A sample of the photothermographic material was exposed for 10^{-4} second to a xenon arc flash and heat processed for 20 seconds on a curved hot block at a temperature of 120°C. A negative image resulted.

A further sample of the unexposed photothermographic element was imagewise exposed for 15 seconds to an ultraviolet light and then overall exposed to a number 2 filtered (KODAK 'Wratten' 25) photoflood lamp for 10 seconds to give a red light exposure. The sample was then overall heat processed for 20 seconds on a curved hot block at a temperature of 120°C. A positive image resulted.

WHAT WE CLAIM IS:-

1. A sensitive photothermographic material which comprises a support coated with a composition containing an oxidation-reduction image-forming system comprising (a) a substantially radiation insensitive silver salt of an organic acid and (b) a non-radiation sensitive reducing agent therefor; (c) a photosensitive dye comprising an *o*-nitro substituted aryl nucleus joined by a methine linkage to a basic heterocyclic nucleus containing an electron-donating oxygen, sulphur or nitrogen atom, said atom and the nitro group being linked by a conjugated chain of carbon atoms; (d) a radiation-sensitive dye comprising a heterocyclic nucleus containing a nitrogen atom carrying an alkoxy or acyloxy group; and (e) a binder.

2. A material according to claim 1 wherein the Dye (c) is according to the Formula I herein.

3. A material according to claim 1 wherein the Dye (c) is one of the Dyes 1 to 8 specified herein.

4. A material according to any of the preceding claims wherein the Compound (d) is of the Formula IIa or IIb herein.

5. A material according to claim 4 wherein the Compound (d) is of one of the Formulae

A to F herein.

6. A material according to any of claims 1 to 3 wherein the Compound (d) is one of the Compounds 1 to 43 specified herein.

7. A material according to any of the preceding claims wherein the silver salt (a) is a salt of a long chain fatty acid having at least 10 carbon atoms.

8. A material according to any of the preceding claims wherein the reducing agent (b) is a bis-β-naphthol.

9. A material according to any of the preceding claims wherein the composition contains an activator-toner.

10. A material according to any of the preceding claims wherein the binder (e) is hydrophobic.

11. A material according to claim 1 substantially as described in any of Examples 1 to 3 herein.

12. A composition for use in making a material as specified in any of claims 1 to 10 which comprises a dispersion of the specified constituents in a solvent.

13. A composition according to claim 12 substantially as described in any of Examples 1 to 3 herein.

14. A method of making a sensitive photothermographic material which comprises coating a support with a layer of a composition according to claim 12.

15. A sensitive photothermographic material made by a method according to claim 14.

16. A method of making a photographic record which comprises imagewise exposing to light a material according to any of claims 1 to 11 and 15 to form a latent image therein and heating the material uniformly to develop the latent image to a visible negative image.

17. A method of making a photographic record which comprises imagewise exposing to ultra-violet radiation a material according to any of claims 1 to 11 and 15, exposing the material overall to light and heating the exposed material uniformly to form a visible direct positive image.

18. A photographic record made by a method according to claims 16 or 17.

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