United States Patent Office **3,813,245**
Patented May 28, 1974

3,813,245

PHOTOCHROMIC COMPOSITION CONTAINING POLYHALOGENATED COMPOUND, SPIROPYRAN COMPOUND AND SENSITIZER AND THE USE THEREOF

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Claims priority, application Great Britain, Sept. 1, 1970, 41,749/70
Int. Cl. G03c *1/52, 5/24*
U.S. Cl. 96—48 R 21 Claims

ABSTRACT OF THE DISCLOSURE

A photographic process wherein a visible image is formed by print-out or optical development in a recording material comprising in intimate admixture a spiropyran compound, an ultra-violet light-sensitive compound capable of producing on exposure with ultra-violet light with the spiropyran a dye salt and as sensitizing agent a compound selected from the group comprising:

(A) organic compounds containing two radicals of different electron-affinity including groups or atoms of different electron-affinity linked to each other through a conjugated system,

(B) organic compounds containing an aromatic nucleus or aromatic ring system in which two adjacent carbon atoms are common to said nucleus or ring system and to an adjacent ring which has no conjugated character and which at one end is linked to the aromatic nucleus or ring system through a carbon-carbon bond and at the other end is linked to said nucleus or ring system through a secondary or tertiary amino group, said organic compounds include those having a said nucleus or ring system in substituted form.

Preferred recording materials contain a spirodinaphthopyran compound, carbon tetrabromide and/or iodoform and as sensitizing agent Michler's ketone or a 2,2,4-trimethyl - 1,2-dihydroquinoline in polystyrene as binding agent.

This invention relates to photographic recording and reproduction of information and to materials suited therefor.

The use of particular spiropyrans in the manufacture of photographic recording materials is known e.g. from the U.S. patent specification 2,953,454 of E. Berman—Nat. Cash Reg., issued Sept. 20, 1960. The spiropyrans described therein are characterized as being reversibly transformable into a colored form by activating electromagnetic energy.

In many applications such reversible transformation is not desirable and therefore efforts have been made to obtain a print-out color image the color of which does not fade by keeping it in the dark or by a further irradiation with electromagnetic radiation differing in wavelength from the radiation originally applied.

In the German patent specification 1,274,655 a recording material has been described by means of which stable print-out dyestuff images can be obtained by using spiropyrans in admixture with a compound that activated with electromagnetic radiation can yield photolytically formed free radicals.

The starting substances for these radicals are preferably halogenated organic compounds.

The recording materials described in the latter patent specification need rather long exposure times with the conventional ultra-violet light sources.

It is an object of the present invention to provide a method for increasing the photosensitivity of recording materials which contain a photosensitive compound that by information-wise exposure to activating electromagnetic radiation yields a dyestuff image by reaction with a spiropyran compound.

It is another object of the present invention to provide a method for making visible or intensifying a latent image or barely visible image produced with said spiropyran and photosensitive compound. Said method is called hereinafter "optical development" for it operates with an overall exposure in the wavelength range of electromagnetic radiation absorbed by dyestuff traces formed in the image-wise exposure.

It is a further object of the present invention to provide photographic materials suited for use in said methods.

It has now been found that the photosensitivity for forming a directly visible image or optical development sensitivity of a recording material containing in intimate admixture:

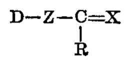
(1) At least one spiropyran compound, and

(2) At least one ultra-violet light-sensitive compound capable of producing on exposure with ultraviolet light with said spiropyran compound a dyestuff salt is increased by applying in working relationship with said mixture at least one organic compound belonging to one of the following classes:

(A) Organic compounds containing two radicals of different electron-affinity (the term radical includes group as well as atoms) linked to each other through a conjugated system

(B) organic compounds containing an aromatic nucleus or aromatic ring system in which two adjacent carbon atoms are common to said nucleus or ring system and to an adjacent ring which has no conjugated character and which at one end is linked to the aromatic nucleus or ring system through a carbon-carbon bond and at the other end is linked to said nucleus or ring system through an electron-donating group such as a secondary or tertiary amino group, said organic compounds include those having said nucleus or ring system in a substituted form.

Useful sensitizing agents of class (A) are those having one of the following general formulae (I), (II), (III), (IV), (V) or (VI):

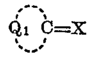


$$D-Z-\underset{\substack{|\\R}}{C}=X$$

(I)

$$D-Z-Y-Z-D$$

(II)



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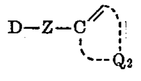

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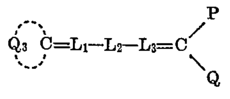

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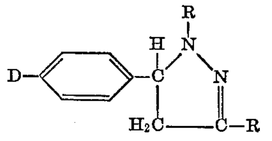


(VI)

wherein:

D represents an electron-donating group e.g. an alkyl (preferably C_1–C_5 alkyl), cycloalkyl or aralkyl substituted amino or hydroxy group, preferably a monoalkyl amino group, a dialkylamino group or an alkoxy group,

Z represents a conjugated system e.g. a polymethine chain carbazole units, can vary between wide limits, say, e.g. between 20 and 95%, taking into account the properties of the compounds used in the preparation of the copolymers and the required sensitizing and/or mechanical properties. In general, the best results are attained with copolymers having a content of vinylcarbazole units between 40 and 90%.

The preparation of suitable poly-N-vinylcarbazoles is described e.g. in the German patent specifications 931,731 filed Mar. 4, 1953, 936,421 filed Feb. 20, 1953, 1,097,680 filed Oct. 15, 1959 all three by B.A.S.F., and 1,158,367 filed July 18, 1962 by Gevaert Photo-Producten N.V., and the U.S. patent specification 2,072,465 of W. Reppe, E. Keyssner and E. Dorrer, issued Mar. 2, 1937. The preparation of poly-N-vinyl-pyrrole proceeds analogously.

The preparation of suitable N-vinylcarbazole copolymers is described in the United Kingdom patent specification 964,875 filed Apr. 21, 1960 by Gevaert Photo-Producten N.V. which specification also contains a preparation receipt for poly(N-allyl carbazole) ($R_1=CH_3$ and $R_2=H$) and for poly(N-propenyl carbazole) ($R_1=H$, $R_2=H$, $A=-CH_2-$).

The poly-N-vinyl indoles are described in the published German patent application 1,906,831 filed Feb. 12, 1969 and 1,917,747 filed Apr. 5, 1969 by I.B.M. Corp. The poly-N-vinyl diphenylamine is described in the published German patent application 2,007,692 filed Mar. 3, 1969 by Xerox Corp. Halogen-substituted poly-N-vinyl carbazoles are described in the published Japanese patent applications 21,875/67 filed June 18, 1964, 25,230/67 filed Oct. 13, 1864, 7,592/68 filed Nov. 27, 1964, 19,751/67 filed June 18, 1964 and 7,591/68 filed Nov. 18, 1964, all by Matsushita Elecric Industrial Co. Ltd.

For illustrative purposes suitable vinyl copolymers containing N-vinyl carbazole units are enumerated in the following Table 2.

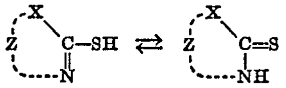
TABLE 2

Copolymer	Mole percent of N-vinyl carbazole
- copolymer of N-vinylcarbazole and vinylidene chloride	85.4
- copolymer of N-vinylcarbazole and 3,3′,5-trimethyl isononylether	93
- copolymer of N-vinylcarbazole and vinyl acetate	88.6
- copolymer of N-vinylcarbazole and isopropenyl acetate	94.5
- copolymer of N-vinylcarbazole and vinylstearate	37.5
- copolymer of N-vinylcarbazole and methylacrylate	67.6
- copolymer of N-vinylcarbazole and ethylacrylate	41
- graft copolymer of N-vinylcarbazole and ethyl-acrylate	90.3
- emulsion polymer of N-vinylcarbazole and polyethyl acrylate	94.5
- copolymer of N-vinylcarbazole and n-butylacrylate	58.3
- copolymer of N-vinylcarbazole and 2-ethylhexylacrylate	51.6
- copolymer of N-vinylcarbazole and acryloxyethyldiethylamine	76.6
- copolymer of N-vinylcarbazole and vinylcinnamate	92.5
- copolymer of N-vinylcarbazole and methylmethacrylate	62.7
- copolymer of N-vinylcarbazole and isobutylmethacrylate	51.8
- copolymer of N-vinylcarbazole and laurylmethacrylate	77.4
- copolymer of N-vinylcarbazole and methacryloxyethyl diethylamine	9.7
- copolymer of N-vinylcarbazole and acrylonitrile	88
- graft copolymer of N-vinylcarbazole and butylaldehyde acetal of polyvinylalcohol	30
- copolymer of N-vinylcarbazole and di(2-dichloroethyl)-vinylphosphonate	82.4
- copolymer of N-vinylcarbazole and styrene	49
- graft copolymer of N-vinylcarbazole and polystyrene	27.3
- copolymer of N-vinylcarbazole and vinylnaphthalene	47.1
- copolymer of N-vinylcarbazole and anthracene-(9,10)	91.5
- copolymer of N-vinylcarbazole and 2-vinylpyridine	31.8
- copolymer of N-vinylcarbazole and 4-vinylpyridine	32.4
- copolymer of N-vinylcarbazole and N-vinylpyrrolidine	69.1
- terpolymer of N-vinylcarbazole, acrylonitrile and styrene	20
- graft copolymer of a terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol with N-vinylcarbazole	29.4
- graft copolymer of a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride with N-vinylcarbazole	55.1

(Q) Organic nitrogen containing compounds having a thiol group or in their tautomeric form a thione group as represented in the following tautomeric structural parts:

$$HS-\overset{|}{C}=\overset{|}{N} \rightleftarrows S=\overset{|}{C}-\overset{|}{N}H$$

Preferably used are heterocyclic compounds having the following tautomeric general formulae:



wherein:

X represents oxygen, sulphur, selenium or the group

$$-\overset{|}{N}R$$

in which R is hydrogen or an organic group e.g. an alkyl group including a substituted alkyl group, preferably a C_1–C_5-alkyl group, and

Z represents the necessary atoms to close a 5- or 6-membered heterocyclic nitrogen containing ring or ring system including such ring or ring system in substituted form e.g. a benzthiazole, benzselenazole, benzoxazole, or benzimidazole ring.

Preferred compounds falling within the scope of class (Q) are e.g.:

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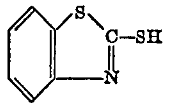

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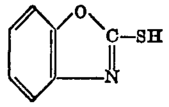

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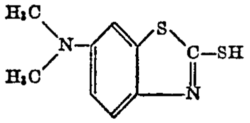

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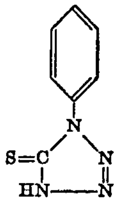

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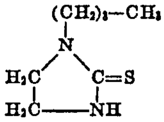

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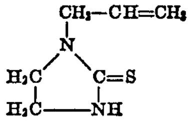

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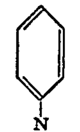

Imidazolidine-4-on-2-thiones, e.g.:

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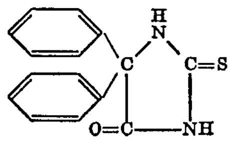

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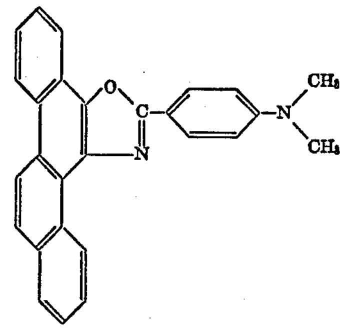

(Ref. J. Prakt. Chem. [2], 157, p. 219 (1941).)

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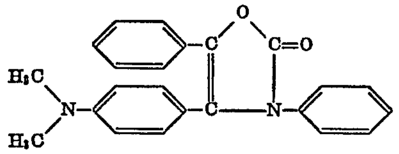

(Ref. Ber. *89*, p. 1748 (1956).)

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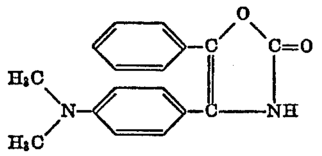

(Ref. Ber. *89*, p. 1748 (1956).)

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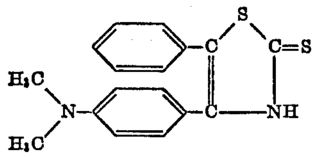

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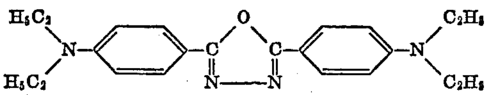

(Ref. U.S. patent specification 3,189,447 of Wilhelm Mengebauer, Martha Tomanek and Hans Behmenburg, issued June 15, 1965.)

Preferred compounds falling within the scope of formula (VI) are described in the United Kingdom patent specification 853,880, filed Dec. 16, 1957 by Kalle AG, e.g.:

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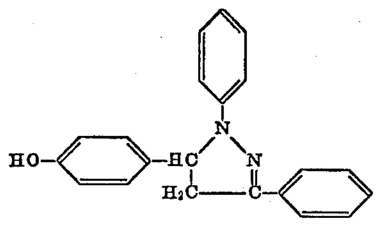

Preferred compounds falling within the scope of formula (V) are merocyanines e.g. those described in the United Kingdom patent specification 1,131,238 filed Nov. 16, 1965 by Eastman Kodak Co. Representatives thereof are e.g.:

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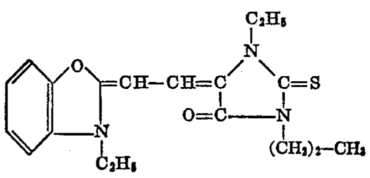

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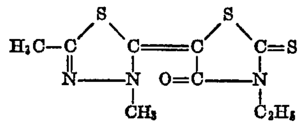

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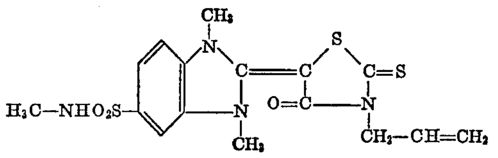

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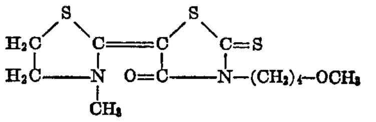

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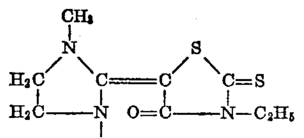

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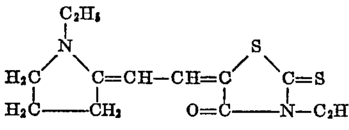

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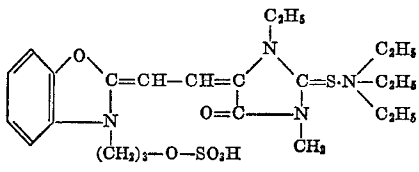

Preferred compounds belonging to class (B) are described e.g. in the Belgian patent specification 727,433 filed Jan. 27, 1969 by Gevaert-Agfa N.V. corresponding with the U.S. patent application Ser. No. 793,881. Representatives thereof are e.g.:

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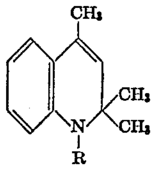

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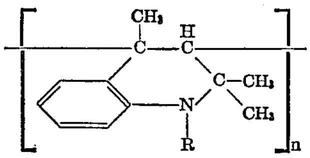


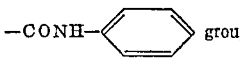
wherein:

n is a positive integer of at least 2, and
R represents hydrogen or an alkyl group including a substituted alkyl group.

Spiropyran compounds suited for photographic image formation according to the present invention are spiropyrans containing at least one pyran ring having in the ortho- and meta-position to the oxygen atom a condensed benzo, naphtho or other higher aromatic polycyclic condensed ring system including these condensed rings or ring systems in substituted state e.g. an anthraceno or a phenanthreno ring system e.g. as present in a spirodibenzopyran, a spirodinaphthopyran, a spirobenzonaphthopyran, a 1,3,3 - trimethylindolinobenzospiropyran, a 1,3,3 - trimethylindolinonaphthospiropyran or such spiropyrans containing condensed aromatic nuclei of the anthracene or phenanthrene type.

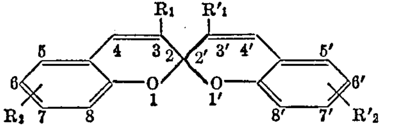
In said spiropyran the pyran rings, the condensed benzo, the condensed higher aromatic rings as well as the 1,3,3-trimethylindolino ring may be substituted.

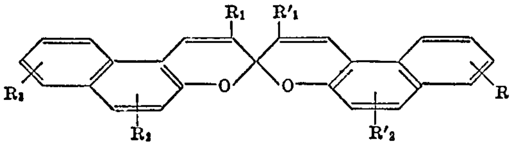
Suitable substituents therefore are e.g. hydrocarbon groups such as alkyl groups, e.g. lower alkyl groups such as methyl, substituted alkyl groups e.g. halogen, or phenyl substituted alkyl groups, alkylene ester groups e.g. a —CH—COOC$_2$H$_6$ group, alkylene carboxyl groups e.g. a —CH$_2$—COOH group, carbonamide groups or substituted carbonamide groups e.g. a

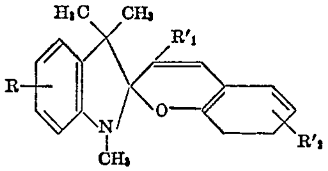


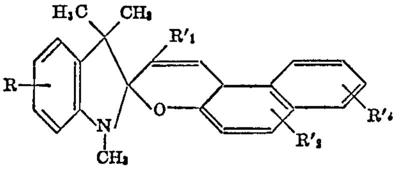
halogen, nitro, hydroxy, alkoxy, aryloxy or a substituent linking the carbon atoms in 3,3′-position in the spiropyran system together e.g. a (CH$_2$)$_n$-chain wherein *n* is 2 or 3.

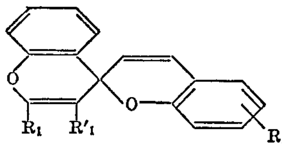
General formulae covering particularly suited spiropyrans are the following:











wherein: R, R$_1$, R′$_1$, R$_2$, R′$_2$, R$_3$ and R′$_3$ represent hydrogen, an aliphatic group including a substituted aliphatic group e.g. a (C$_1$–C$_{20}$) alkyl group including such an alkyl group in substituted form, more particularly a methyl, ethyl, propyl, amyl or hexadecyl group or halogen substituted alkyl group, halogen, nitro, hydroxy, an alkoxy or aryloxy group, a phenyl group or a substituted phenyl group, piperidyl, an alkylene ester group e.g. a

—CH$_2$—COOC$_2$H$_5$

group, an alkylene carboxyl group e.g. a —CH$_2$—COOH group, a carbonamide group or a substitutel carbonamide group e.g. a

or R$_1$ and R′$_1$ together represent a —(CH$_2$)$_n$-chain wherein n=2, or 3 to link the carbon atoms in the 3 and 3′ positions together.

Suited spiropyran compounds and their preparation are described in the published German patent applications 1,274,655 filed Dec. 15, 1965 by Telefunken Patentverwertungs G.m.b.H., 1,269,665, 1,286,110, 1,286,111 and 1,286,112 all filed Sept. 30, 1966 by Telefunken Patentverwertungs G.m.b.H., and by W. Dilthey, Berres, Hölterkoff, Wübken, J. Pr. Ch. [2] *114*, 187 (1926), by C. F. Koelsch anl W. R. Workman in J.A.C.S. *74* 6288 (1952) and in J. Chem. Soc. (1934), 1571 by I. M. Heilbron and G. F. Howard.

Preferred spiropyran compounds are spirodinaphthopyrans and spirobenzonaphthopyrans including such compounds wherein the naphtho- and/or benzo ring(s) is (are) substituted.

An illustrative list of particularly useful spiropyran compounds is given in the following Table 1.

TABLE 1

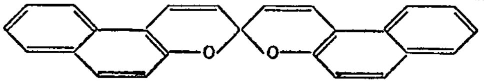
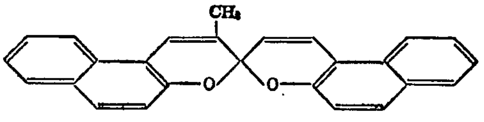
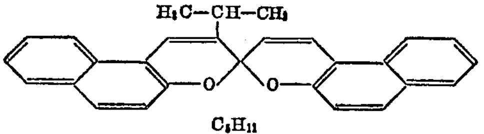
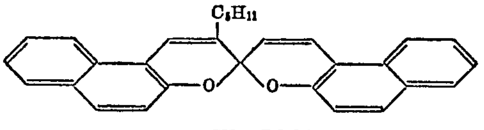
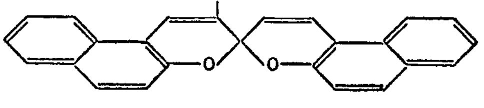
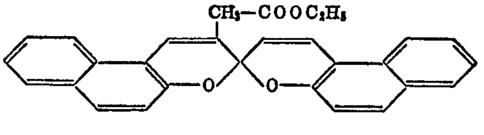
	Spiropyran compound	Melting point (° C.)
1		257
2		204
3		208
4		185
5		164
6		166

TABLE 1—Continued

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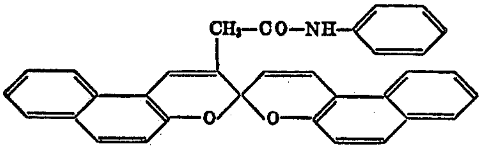
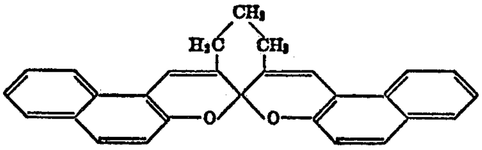
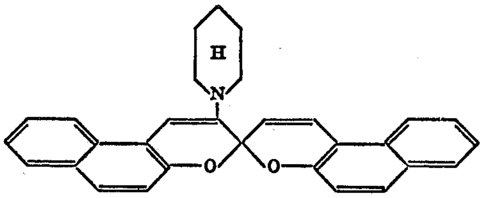
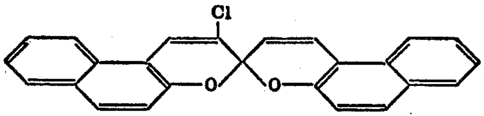
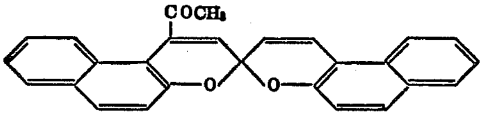
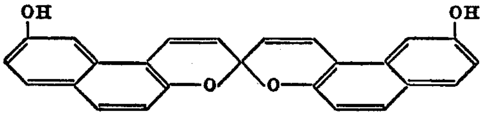
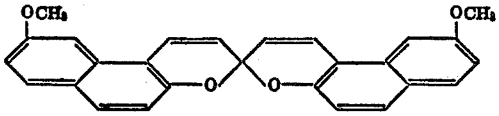
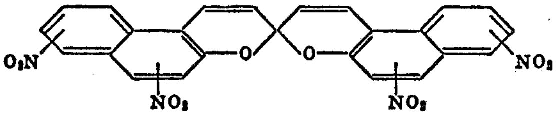
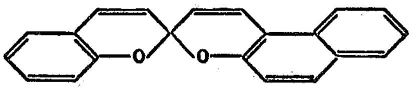
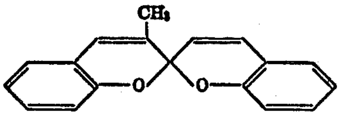
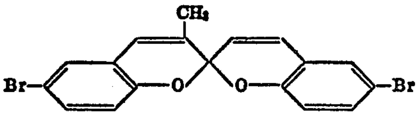
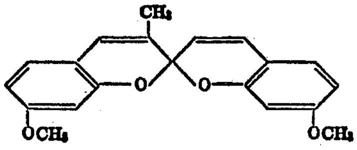
7		210
8		
9		140
10		180
11		260
12		>260
13		>260
14		>260
15		168
16		110
7		163
18		110

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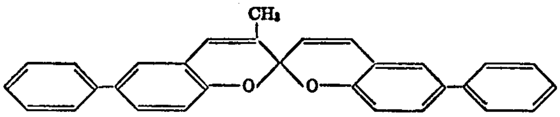
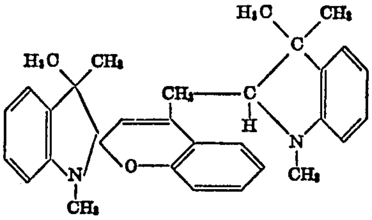
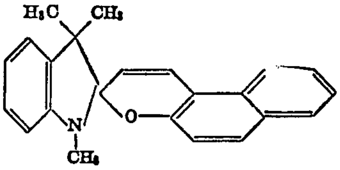
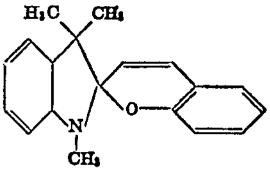
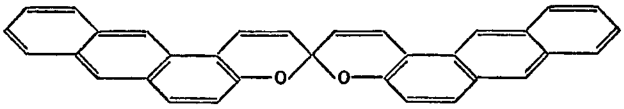
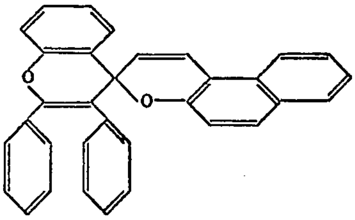
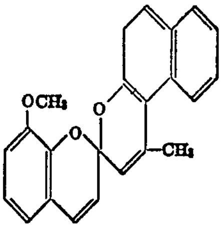
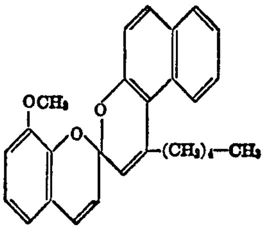
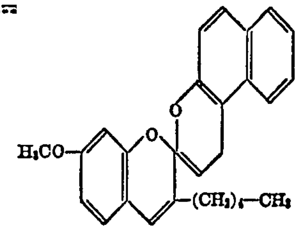
19		185
20		206
21		180
22		88
23		>260
24		173
25		193
26		158
27		144

TABLE 1—Continued

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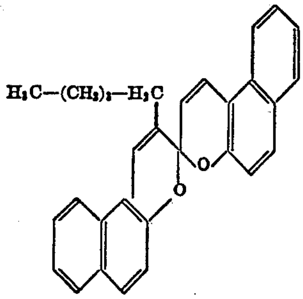
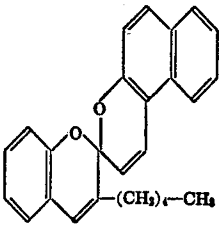
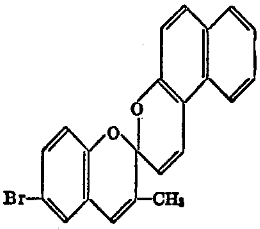
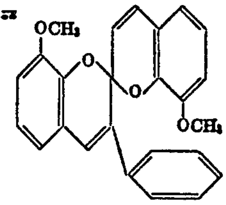
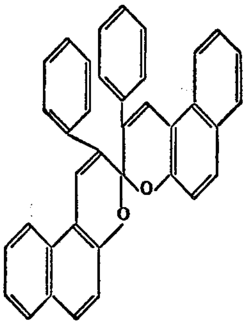
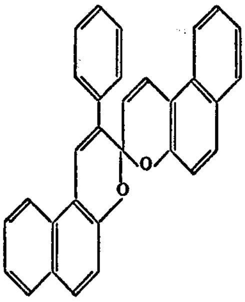
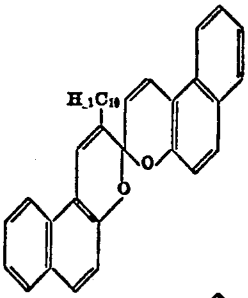
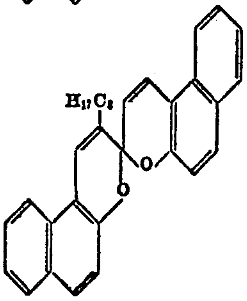
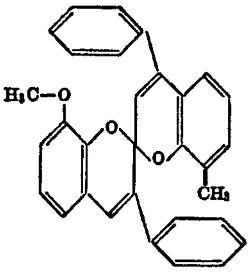
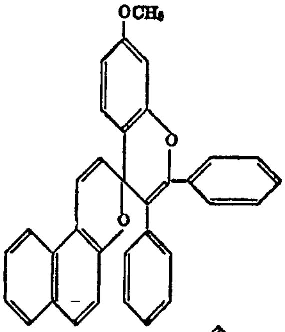
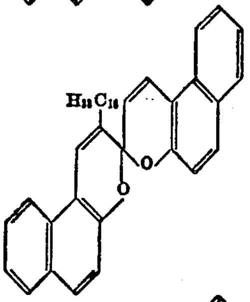
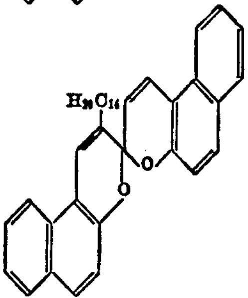
28		180
29		160
30		112
31		120
32		±200
33		248

TABLE 1—Continued

	Spiropyran compound	Melting point (° C.)
34		152
35		160
36		±250
37		173
38		133
39		146

In order to illustrate in more details the preparation of the diarylo spiro-pyran compounds and the indolinearylospiropyran compounds the following preparation receipts are given:

PREPARATION 1

Preparation of 3-methyldi-β-naphthospiropyran (compound 2 of Table 2)

In a 2-litre three-necked flask, fitted with a reflux condenser and a gas inlet tube reaching nearly the bottom of the flask are introduced:

Ethanol	litre	1
Butanone	(0.25 mole) ml.	22
2 hydroxy-1-naphthaldehyde	(0.5 mol) g.	86

The flask is shaped until partial dissolution of the ingredients. Dry hydrogen chloride gas is introduced at a rate which allows complete absorption and the start of ethanol reflux. Thereupon the already strongly blue colored mixture is cooled down in a mixture of ice and sodium chloride and the introduction of hydrogen chloride gas continued until saturation. In the reaction mixture green crystals of pyrylium salt are formed and the crystallization allowed to proceed overnight in a refrigerator.

The formed pyrylium salt is separated by suction, is washed with ethanol and thereupon brought into suspension in 300 ml. of ethanol.

Whilst stirring a 10% by weight aqueous solution of ammonium hydroxide is added until the mixture is definitely alcaline. During that operation the mixture becomes colorless.

The obtained crystalline product is separated by suction, washed with water and dried.

Finally the spiropyran compound is recrystallized from 600 ml. of benzene and again separated and dried under reduced pressure at 50–60° C. Yield: 45 g. Melting point: 204° C.

PREPARATION 2

Preparation of 1,3,3-trimethylindolinobenzopyrlospiran (compound 22 of Table 2)

In a 100 ml. flask fitted with a reflux condenser are introduced the following ingredients:

Salicylaldehyde	(0.03 mole) g.	3.7
1,3,3 - trimethyl - 2 - methylene indolamine	(0.03 mole) g.	5.1
Ethanol	ml.	90

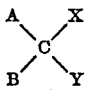
The solution is boiled under reflux for a period of 2 hours. Thereupon the mixture is cooled down and filtered.

To the filtrate water is added for separation of a solid product. The solid is separated by suction, washed with water and dried under vacuum conditions.

The spiran compound is recrystallized from 15 ml. of hexane.

Yield: 5 g. Melting point: 93–94° C.

The compound capable of producing a dye salt with a spiropyran on exposure to activating electromagnetic radiation is for use according to the present invention preferably an organic polyhalogen compound of which a halogen containing radical can be photolytically separated. Compounds possessing that property are within the scope of the following general formula:



wherein each of A, B, X and Y are halogen atoms of the group of chlorine, bromine or iodine, or

wherein one of said radicals A, B, X or Y represents an alkyl group, including a substituted alkyl group e.g. a halogen substituted alkyl radical, a hydroxylalkyl radical or an aralkyl radical e.g. a benzyl radical, an aryl group, a substituted aryl group or an aroyl group and the other radicals chlorine, bromine or iodine, or wherein at least two of said radicals A, B, X or Y represent an aromatic acyl group e.g. a benzoyl group and the other radicals chlorine, bromine or iodine.

Suitable representatives falling within the scope of that general formula are organic halides such as carbon tetrabromide, bromoform, iodoform, hexachloroethane, hexabromoethane, pentabromoethane, 1,1,2,2-tetrabromoethane, α,α,α-tribromoacetophenone and tribromoethanol.

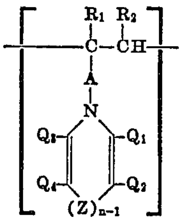
The amount of sensitizing agent is not critical.

A rather small amount of sensitizing agent with respect to the spiropyran compound may be used e.g. 0.0005 g. to 0.10 g. of sensitizing agent to 0.005 g. to 0.2 g. of spiropyran compound.

The spiropyran compound(s) are further preferably used in admixture with a 5- to 20-fold amount by weight of photosensitive organic halogen compound such as carbon tetrabromide. This ratio is, however, not limitative since useful results can be obtained with e.g. the spiropyran and photosensitive polyhalogen compound in a ratio by weight in the range of 1:1 to 1:50.

The sensitizing agents used according to the present invention may be applied as the sole sensitizing agents or in combination with one or more sensitizing compounds belonging to one of the following classes:

(P) Polymeric compounds containing recurring units of the following general structure:



wherein:

Z represents a sulphur atom or a single bond,

A represents a single bond or a divalent hydrocarbon group e.g. a —CH_2— group,

R_1 represents hydrogen or a lower alkyl radical, e.g. a methyl radical,

R_2 represents hydrogen or a lower alkyl radical, e.g. a methyl or an ethyl radical,

Q_1 and Q_2 each represent a hydrogen atom or together the necessary atoms to close an adjacent carbocyclic ring or ring system including such ring or ring system in substituted form, preferably an aromatic ring (e.g. a benzene ring) including a substituted aromatic ring e.g. a halogen substituted (chlorine, bromine or iodine substituted) benzene ring,

Q_4 and Q_3 each represent a hydrogen atom or together the necessary atoms to close an adjacent carbocyclic nucleus or ring system including such a ring or ring system in substituted form, preferably an aromatic ring (e.g. a benzene ring) including a substituted aromatic ring e.g. a halogen substituted (chlorine, bromine or iodine substituted) benzene ring, and

n represents 1 or 2.

The N-vinyl polymers and copolymers of class (P) can be prepared by application of one of the various known polymerization procedures, e.g., by pearl- or emulsion polymerization or by polymerization in solution, whereby the initiation of the polymerization can occur by free radical, by ion formation, or by radiation e.g., with actinic light. It is to be noted that the polymerization degree is not critical and can vary between wide limits. As far as the copolymers are concerned, it is further to be noted that the content of groups corresponding to the general formula given hereinbefore is not critical and, as shown furtheron in the table of copolymers containing N-vinylcarbazole units, can vary between wide limits, say, e.g. between 20 and 95%, taking into account the properties of the compounds used in the preparation of the copolymers and the required sensitizing and/or mechanical properties. In general, the best results are attained with copolymers having a content of vinylcarbazole units between 40 and 90%.

The preparation of suitable poly-N-vinylcarbazoles is described e.g. in the German patent specifications 931,731 filed Mar. 4, 1953, 936,421 filed Feb. 20, 1953, 1,097,680 filed Oct. 15, 1959 all three by B.A.S.F., and 1,158,367 filed July 18, 1962 by Gevaert Photo-Producten N.V., and the U.S. patent specification 2,072,465 of W. Reppe, E. Keyssner and E. Dorrer, issued Mar. 2, 1937. The preparation of poly-N-vinyl-pyrrole proceeds analogously.

The preparation of suitable N-vinylcarbazole copolymers is described in the United Kingdom patent specification 964,875 filed Apr. 21, 1960 by Gevaert Photo-Producten N.V. which specification also contains a preparation receipt for poly(N-allyl carbazole) (R_1=CH_3 and R_2=H) and for poly(N-propenyl carbazole) (R_1=H, R_2=H, A=—CH_2—).

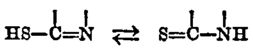
The poly-N-vinyl indoles are described in the published German patent application 1,906,831 filed Feb. 12, 1969 and 1,917,747 filed Apr. 5, 1969 by I.B.M. Corp. The poly-N-vinyl diphenylamine is described in the published German patent application 2,007,692 filed Mar. 3, 1969 by Xerox Corp. Halogen-substituted poly-N-vinyl carbazoles are described in the published Japanese patent applications 21,875/67 filed June 18, 1964, 25,230/67 filed Oct. 13, 1864, 7,592/68 filed Nov. 27, 1964, 19,751/67 filed June 18, 1964 and 7,591/68 filed Nov. 18, 1964, all by Matsushita Elecric Industrial Co. Ltd.

For illustrative purposes suitable vinyl copolymers containing N-vinyl carbazole units are enumerated in the following Table 2.

TABLE 2

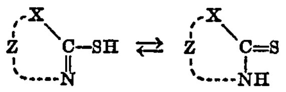
Copolymer	Mole percent of N-vinyl carbazole
- copolymer of N-vinylcarbazole and vinylidene chloride	85.4
- copolymer of N-vinylcarbazole and 3,3′,5-trimethyl isononylether	93
- copolymer of N-vinylcarbazole and vinyl acetate	88.6
- copolymer of N-vinylcarbazole and isopropenyl acetate	94.5
- copolymer of N-vinylcarbazole and vinylstearate	37.5
- copolymer of N-vinylcarbazole and methylacrylate	67.6
- copolymer of N-vinylcarbazole and ethylacrylate	41
- graft copolymer of N-vinylcarbazole and ethyl-acrylate	90.3
- emulsion polymer of N-vinylcarbazole and polyethyl acrylate	94.5
- copolymer of N-vinylcarbazole and n-butylacrylate	58.3
- copolymer of N-vinylcarbazole and 2-ethylhexylacrylate	51.6
- copolymer of N-vinylcarbazole and acryloxyethyldiethylamine	76.6
- copolymer of N-vinylcarbazole and vinylcinnamate	92.5
- copolymer of N-vinylcarbazole and methylmethacrylate	62.7
- copolymer of N-vinylcarbazole and isobutylmethacrylate	51.8
- copolymer of N-vinylcarbazole and laurylmethacrylate	77.4
- copolymer of N-vinylcarbazole and methacryloxyethyl diethylamine	9.7
- copolymer of N-vinylcarbazole and acrylonitrile	88
- graft copolymer of N-vinylcarbazole and butylaldehyde acetal of polyvinylalcohol	30
- copolymer of N-vinylcarbazole and di(2-dichloroethyl)-vinylphosphonate	82.4
- copolymer of N-vinylcarbazole and styrene	49
- graft copolymer of N-vinylcarbazole and polystyrene	27.3
- copolymer of N-vinylcarbazole and vinylnaphthalene	47.1
- copolymer of N-vinylcarbazole and anthracene-(9,10)	91.5
- copolymer of N-vinylcarbazole and 2-vinylpyridine	31.8
- copolymer of N-vinylcarbazole and 4-vinylpyridine	32.4
- copolymer of N-vinylcarbazole and N-vinylpyrrolidine	69.1
- terpolymer of N-vinylcarbazole, acrylonitrile and styrene	20
- graft copolymer of a terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol with N-vinylcarbazole	29.4
- graft copolymer of a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride with N-vinylcarbazole	55.1

(Q) Organic nitrogen containing compounds having a thiol group or in their tautomeric form a thione group as represented in the following tautomeric structural parts:



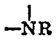
$$HS-\overset{|}{C}=\overset{|}{N} \rightleftarrows S=\overset{|}{C}-\overset{|}{N}H$$

Preferably used are heterocyclic compounds having the following tautomeric general formulae:



wherein:

X represents oxygen, sulphur, selenium or the group



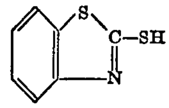
$$-\overset{|}{N}R$$

in which R is hydrogen or an organic group e.g. an alkyl group including a substituted alkyl group, preferably a C_1–C_5-alkyl group, and

Z represents the necessary atoms to close a 5- or 6-membered heterocyclic nitrogen containing ring or ring system including such ring or ring system in substituted form e.g. a benzthiazole, benzselenazole, benzoxazole, or benzimidazole ring.

Preferred compounds falling within the scope of class (Q) are e.g.:

(28)



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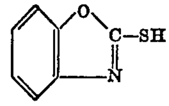

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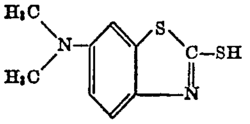

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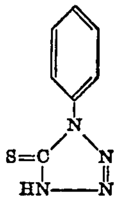
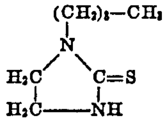
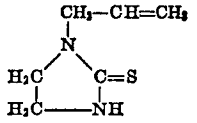


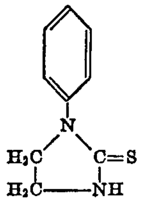
(32)



(33)

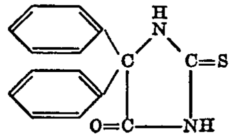


(34)



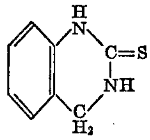
Imidazolidine-4-on-2-thiones, e.g.:

(35)



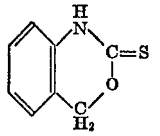
Tetrahydro pyrimidine-2-thiones, e.g.:

(36)

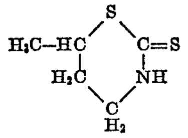


Tetrahydro- and dihydro-oxazine-2-thiones and thiazine-2-thiones, e.g.:

(37)

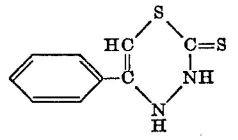


(38)



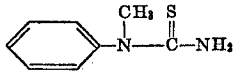
1,3,4-dihydro thiadiazine-2-thiones, e.g.:

(39)



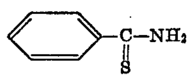
Thiourea compounds including substituted derivatives preferably N-phenyl thiourea compounds, e.g.:

(40)



Thioamides, e.g.:

(41)



It is remarkable that most of the suitable sensitizing mercapto compounds are generally known black-toning agents in the silver complex diffusion transfer process.

(R) Inorganic compounds producing photoelectrons under the influence of activating electromagnetic radiation and having a basic or amphoteric character e.g. photoconductive zinc oxide and PbO.

In case photoconductive zinc oxide is used as sensiting substances the recording layer contains preferably from 5 to 50 parts by weight of zinc oxide dispersed in 100 parts by weight of binding agent containing the spiropyran compound(s) preferably in an amount of 1 to 50 parts by weight and the photosensitive reactant for forming the dyestuff salt e.g. a photosensitive organic halogen compound such as carbon tetrabromide and/or iodoform in an amount of 10 to 250 parts by weight.

As a further constituent the photosensitive recording layer according to the present invention may contain a film-forming binder. For that purpose preferably hydrophobic polymers are used that shield as much as possible the ingredients from a direct contact with the atmosphere and more especially from oxygen.

Particularly suitable binders for use in the present invention are hydrophobic polymers and copolymers e.g. containing styrene, vinyl acetate, acrylonitrile, acrylic acid ester, methacrylic acid ester, N-vinylcarbazole or butadiene units, hydrophobic cellulose derivatives, phenoxy resins or polycondensates of the polyester type e.g. polycarbonates.

These polymers can be used in a mixture for improvement of the mechanical strength or adhering power of the recording layer to its support when no self-supporting layer is produced.

In order to diminish the rate of spontaneous thermal colour formation over long periods of time as might be encountered during storage of the photographic material and processing of the photographic materials so-called anti-foggants may be added to the photosensitive composition. Suitable anti-foggants include triaryl compounds of group V elements e.g. triphenylstilbine and sterically hindered phenols e.g. 2,6-di-tert.butyl p-cresol and other reducing or atmospheric oxygen accepting agents. Triphenylstilbine and analogous compounds for the purpose of the present invention are described in the United Kingdom patent specification 1,071,104, filed Aug. 14, 1964 by Horizons Inc.

A dry photographic coating containing the above mentioned ingredients may be formed by dissolving the binding agent(s) in a suitable inert solvent which acts as dispersing or dissolving medium for the other ingredients and which is removed from the coating composition by evaporation leaving a solid photographic recording layer on a properly chosen support. The supports may be of any kind encountered in silver halide photographic materials e.g. paper and film supports.

In order to realize the highest sensitivity, it is desirable to coat the recording layers in the absence of oxygen or to keep them before the exposure in an oxygen-free environment.

The photosensitive organic polyhalogen compounds that in exposed state form with a spiropyran compound a dyestuff salt are normally only sensitive in a wavelength range between 400 and 250 nm.

Various sensitizing agents of the enumerated classes sensitize the recording composition in its inherent sensitivity range and it is assumed that they may also be considered as chemical sensitizing agents for they may chemically interact with photoradicals formed during the exposure.

A choice of a proper combination of sensitizing agents that are active for extending the sensitivity in the visible spectrum of the print-out recording composition used in the present invention makes it possible to apply white or colored light in the information-wise exposure.

By using organic spectral sensitizing agents e.g. that are within the scope of the definition of class (A) and that have in their structure a conjugated system of sufficient length it is possible to extend the spectral sensitivity into the visible light spectrum and even into the infrared.

The spectral sensitization over the whole visible spectrum opens the possibility to produce print-out multicolor prints by means of one and same recording material. So, on using a recording material containing superposed recording layers sensitized respectively in the red, green, and blue region of the spectrum and containing the proper dye forming combination superposed cyan, magenta and yellow part images can be produced that offer a full reproduction of the multicolor original used in the information-wise exposure.

The recording materials sensitized according to the present invention are suited to produce print-out images of different color according to the type of spiropyran compound applied.

The stabilization of the obtained prints may proceed by washing out the residual free radical generator with a suitable solvent or sorbent mixture e.g. a hydrocarbon liquid such as petroleum ether optionally mixed with acetone, or by simply evaporating it by raising the temperature when the compound involved is sufficiently volatile. For the latter purpose and the high photosensitivity, carbon tetrabromide or a mixture of carbon tetrabromide and iodoform is preferred.

According to a preferred recording and reproduction process of the present invention the information-wise exposure is carried out in such a way that first a latent image is produced which is transformed into a visible dye image by means of a so-called "optical development."

The optical development proceeds by exposing the recording layer containing the latent or barely visible image over its entire surface with visible radiation which lies in the spectral absorption band of the products formed by the image-wise exposure and image-wise interaction of the photoexposed ingredients (1) and (2) of the mentioned photosensitive composition. In the overall exposure no exposure light is applied to which the photosensitive polyhalogen compound is inherently sensitive since thereby the effect of the image-wise exposure is masked by an overall coloration. It is advantageous to use in the optical development exposure a cut-off filter absorbing all the light corresponding with the wavelength range that is inherently absorbed by the ingredients of the non-previously exposed recording layer.

The optical development effect is markedly speeded up and the image density increased by applying heat e.g. supplied by contact with a hot body or through infrared radiation during the overall exposure to visible light.

The increase of speed of the optical development is very outspoken by the use of poly-N-vinyl carbazole and the copolymer containing N-vinyl carbazole units.

The optical development speed obtains a particularly high value by the use of Michler's ketone or analogues in combination with the mercapto compounds of class (Q). The addition of a triarylstibine such as triphenylstibine to that combination intensifies the image density obtained by the optical development procedure.

It is assumed that during the exposure applied in the optical development at least a part of the overall applied light energy is visible light, absorbed by a dyestuff salt having the pyrylium structure when using a diarylo spiropyran or having an indolinium salt structure when using an indolino-arylospiropyran. Said salt seems to act as a spectral sensitizing agent for a chemical reaction between the photosensitive polyhalogen compound producing the necessary radicals for forming the dyestuff salt with the spiropyran.

In a particular preferred composition for forming print out as well as optical developable prints a mixture of CBr_4 and CHJ_3 yielding a super additive sensitivity effect is used.

According to an alternative embodiment of the optical development technique the recording material is first overall exposed to electromagnetic radiation to produce non-differentially over the whole recording layer latent dyestuff centres that are afterwards optically developed information-wise by a sufficiently strong information-wise exposure in the absorption band of the dyestuff centres. Optionally the information-wise exposure proceeds simultaneously with an overall heating e.g. effected by an overall infra-red light exposure.

Instead of applying an overall pre-exposure to form the dyestuff centres these dyestuffs may be added e.g. applied by imbibition (diffusion) in minor amounts to the recording layer composition to act as optical development nuclei for the dye image formation by image-wise exposure.

According to a special embodiment the spiropyrans are formed in the non-exposed recording layer composition "in situ" by starting from the corresponding pyrylium and indolinium salts and adapting the pH in a proper way to obtain the spiropyrans that may be considered as the dyestuff precursors of the pyrylium and indolinium salts, respectively.

The information-wise exposure applied in the present invention may be a contact exposure of the direct or reflex type and also an optical projection exposure as used e.g. in an optical enlarging apparatus. The information-wise exposure need not be simultaneous in all part of the recording material. The exposure may be progressive in one continuous step as e.g. in sound track recording or in sucessive intermittent steps provided that the required information-wise change is obtained. Thus the recording material may be scanned with an image-wise modulated radiant energy spot of high intensity e.g. a laser beam, or the material may be progressively exposed through a slit, e.g. is exposed to copying light of a tubular lamp that is given a translation movement along the original.

A recording material of the present invention being suited for the recording of information in the form of modulated ultraviolet radiation can be used in X-ray and electron-beam recording. X-ray beams can be absorbed in high energy absorbing substances and create by means of them so-called secundary photons, e.g., of the ultraviolet radiation energy band and photo-electrons that are absorbed by the photosensitive polyhalogen compound forming through its photoradicals a dyestuff salt with the spiropyran. Substances for high energy absorption that may be incorporated in the recording element contain the elements, lead, mercury, bismuth, barium and/or tungsten. Lead compounds that themselves are photosensitive are preferred e.g. lead monoxide, lead bromide and lead iodide.

Suitable light sources for use in a recording method of the present invention are ultra-violet light sources, xenon-gas lamps, incandescent bulbs, the light of the sun and flash lamps. In the overall exposure for the optical development an infra-red lamp emitting also in the visible spectrum is preferably used.

Electron beam and laser beam recording proceed with the apparatus suited for that purpose and known to those skilled in the art.

Recording materials of the present invention are very versatile in that they by the use of a proper sensitizing agent can be applied for continuous tone or halftone reproduction. They can offer very contrasty images so that they are very suited for the reproduction of line and screen type originals and find a successful use in a great variety of graphic art applications. The recording materials of the present invention are for their very high resolving power particularly suited for microfilm reproduction and high precision image rendering as e.g. in the production of optical micromask masters used in the manufacturing of microelectronic circuitry.

The reflex-exposure properties of the present recording materials make them very useful in the document reproduction sector since they offer in a reflex-contact exposure print-out images of a sufficiently intense spectral density.

According to a special application a recording layer as described herein is used in conjunction with a magnetic recording layer and is more particularly applied at the rear side of a flexible tape support carrying the magnetic recording layer. Using such a material a sound track is formed in the magnetic recording layer and a visual text image corresponding with the sound track photographed on the recording layer of the present invention.

Such a recording material thus allows the storing of optical and acoustic signals and makes it possible to reproduce both informations simultaneously.

The present invention is illustrated by the following examples without, however, limiting it thereto. The percentages are by weight unless otherwise indicated.

EXAMPLE 1

Preparation of sample A

500 mg. of carbon tetrabromide and 10 mg. of the spiropyran compound No. 1 of Table 1 were dissolved in 8 ml. of a 5% solution of polystyrene in methylene chloride. The obtained solution was applied with a layer thickness of 0.1 mm. onto a non-subbed polyethylene terephthalate support.

The coating was dried for 30 min. at 50° C. in the dark.

Preparation of sample B

200 mg. of carbon tetrabromide, 200 mg. of iodoform and 10 mg. of the spiropyran compound No. 1 of Table 1 were dissolved in 8 ml. of a 5% solution of polystyrene in methylene chloride. The obtained solution was coated in the same way as described for sample A.

Preparation of sample C

500 mg. of carbon tetrabromide, 10 mg. of spiropyran compound No. 1 of Table 1 and 5 mg. of p,p'-dimethyl-

aminobenzophenone (Michler's ketone) were dissolved in 8 ml. of a 5% solution of polystyrene in methylene chloride. The obtained solution was applied as described for sample A.

Preparation of sample D

500 mg. of carbon tetrabromide, 200 mg. of iodoform, 10 mg. of the spiropyran compound No. 1 of Table 1 and 5 mg. of p,p'-dimethylaminobenzophenone were dissolved in 8 ml. of a 5% solution of polystyrene in methylene chloride. The obtained solution was applied as described for sample A.

Print-out processing of samples A and B

Sample A was exposed through a grey wedge with constant 0.15 for 2 min. by means of a high pressure mercury vapor lamp sold by Philips' Gloeilampenfabrieken N.V., The Netherlands as HPL lamp-80 w. (trade name). During the exposure the lamp was placed at a distance of 15 cm. of the recording layer.

A cyan colored wedge print containing 2 to 3 visible steps was obtained.

The exposed recording layer was stabilized against background coloration by a heat treatment at 120° C. for 10 min.

The sample B was exposed and processed in the same way as sample A.

A cyan colored wedge print containing 5 visible steps was obtained.

Print-out processing of samples C and D

Both of the samples C and D were in the same way exposed as the samples A and B.

In the recording layer of sample C a cyan colored wedge print containing 7–8 visible steps was obtained.

In the recording layer of sample D a cyan colored wedge print containing 10 visible steps was obtained. A same stabilization treatment as for the samples A and B was applied.

Optical development processing of sample B

The recording layer of sample B was at a distance of 10 cm. for 3 sec. exposed through a negative line image transparency with a HPL lamp-80 w. (trade name). Thereupon the image-wise exposed film was subjected to an overall exposure by means of an infra-red lamp of 250 w. (sold by Bie and Berntsen, 35 Pilestraede, Copenhagen, Denmark) emitting also in the visible part of the spectrum. Between the infrared-lamp and the recording layer a cut-off filter was placed absorbing all the light with a wavelength smaller than 540 nm. (Corning C.S. 3–67).

Within an overall exposure period of 4 min. a cyan image having opposite image values with respect to the original and having an optical density (D) of about 1 was obtained. The obtained image was stabilized by heating at 120° C. for 10 min.

Optical development processing of samples C and D

The recording layer of sample C was exposed image-wise for 2 sec. through the same negative line-image transparency as used in the exposure of sample B herein also applying the same exposure distance and high pressure mercury vapor lamp.

The latent image formed was optically developed to a visible image by means of an overall exposure of 5 min. effected under the same circumstances as described for sample B.

A cyan colored image corresponding with the image-wise exposed areas and having an optical density of about 1 was obtained. Without the use of Michler's ketone a same result could only be obtained by means of an imagewise exposure of 2 min.

The recording layer of sample D was exposed image-wise for 1 sec. under the exposure conditions as described for sample C and thereupon overall exposed in the same way, the overall exposure lasting, however, only 1 min. Corresponding with the image-wise exposed areas a cyan image of an optical density 1 and free from background coloration (fog) was obtained.

EXAMPLE 2

Photosensitive compositions consisting of an intimate mixture of 500 mg. of carbon tetrabromide, 5 mg. of Michler's ketone, 10 mg. of one of the spiropyran compounds represented in Table 1 and 8 ml. of a 5% solution of polystyrene in methylene chloride were coated separately at a thickness of 0.1 mm. onto non-subbed polyethylene terephthalate film strips. The thus obtained recording layers containing each a different spiropyran compound were dried during 30 min. at 50° C. in the dark.

In order to determine the direct print-out sensitivity the different layers were subjected to a contact-exposure through a grey wedge (constant 0.15) using a high pressure mercury vapor bulb, HP-80 w. (trade name of Philips' Gloeilampenfabrieken N.V., The Netherlands) placed at a distance of 10 cm. and operating with an exposure time of 2 min.

In order to determine the optical development sensitivity a first relatively short image-wise exposure with the same high pressure mercury vapor bulb as used in the print-out exposure and placed at a distance of 10 cm. was applied. The image-wise exposure being a contact exposure through a line image transparency was of such duration that a latent image or barely visible image was obtained starting from which in the optical development a visible image without significant background coloration was obtained.

The overall-exposure applied in the optical development was effected by means of a 250 w.-infrared lamp (Bie and Berntsen, Copenhagen, Denmark) through a cut-off filter absorbing substantially all the light with a wavelength smaller than 540 nm.

The results obtained with said different layers are listed hereinafter in Table 3.

In said Table 3 the print-out sensitivity is illustrated by means of the amount of reproduced wedge steps obtained under the above mentioned exposure conditions.

For the optical development the duration of the image-wise exposure and the duration of the overall exposure are given by means of which images with a maximum optical density (D) between 0.5 and 1 without significant background coloration (fog) were obtained.

The stabilization of the obtained images was effected by heating the exposed recording layers at 120° C. for 5 to 10 min.

TABLE 3

Number of the spiropyran compound of Table 1	Number of the by print-out reproduced wedge steps	Optical development: Duration of the image-wise exposure (sec.)	Optical development: Duration of the overall exposure (min.)
1	9	2	5.
2	7–8	2	7.
3	5–6	1–2	15.
4	7	3	5.
5	6–7	3	8.
6	7	3	7.
7	4–5	1–2	5 (fog).
8	4–5	5	10 ($D<0.5$).
9	4–5	10	10.
10	4–5	10	15($D<0.5$).
11	4–5	4	6($D<0.5$).
12	3	5	10($D<0.5$).
13	8–9	2	10.
14	2–3	10	Weak effect.
15	7–8	3	5.
16	2–3	10	Weak effect.
17	2	10	Do.
18	2	10	Do.
19	5–6	5	15.
20	3	10	Weak effect.
21	4–5	10	Do.
22	4–5	10	Do.
23	5–6	10	Do.

EXAMPLE 3

Photosensitive compositions consisting of an intimate mixture of 200 mg. of carbon tetrabromide, 200 mg. of iodoform, 10 mg. of one of the spiropyran compounds represented in Table 1. 5 mg. of Michler's ketone and 8 ml. of a 5% solution of polystyrene in methylene chloride were coated separately at a thickness of 0.1 mm. onto non-subbed polyethylene terephthalate film strips. The thus obtained recording layers were treated as in Example 2. In Table 4 the results of their print-out and optical development characteristics are listed.

TABLE 4

Number of the spiropyran compound of Table 1	Number of the by print-out reproduced wedge steps	Optical development	
		Duration of the image-wise exposure (sec.)	Duration of the overall exposure (min.)
1	11–12	0.5	1–2
2	10	0.8	1–2
4	9	1	2
5	7–8	1	5
6	8–9	0.5	2
7	10–11	0.5	1.5
9	6–7	3	5
13	10	2	3
15	8–9	2	3
18	4–5	2	10
19	6–7	1	6
25	7	1	5
26	8	1	5
27	11–12	1	1–2
29	10	1	2
30	7	1	5

EXAMPLE 4

Photosensitive compositions consisting of an intimate mixture of 500 mg. of carbon tetrabromide, 10 mg. of di-β-naphthospiropyran (compound 1 of Table 1) and 5 mg. of one of the sensitizing compounds indicated by number in the description and 8 ml. of a 5% solution of polystyrene in methylene chloride were coated separately at a thickness of 0.1 mm. onto non-subbed polyethylene terephthalate film strips. The thus obtained recording layers containing each a different sensitizing agent were dried during 30 min. at 50° C. in the dark.

The obtained samples were tested on print-out and optical development sensitivity as explained in Example 2. The results of these tests are listed in Table 5.

TABLE 5

Number of the sensitizing agent	Number of the by print-out reproduced wedge steps	Optical development	
		Duration of the image-wise exposure (sec).	Duration of the overall exposure for D=1 (min.)
	3	120	(1)
5	5–6	10	5
6	9–10	1	2.5
10	6	3	5
10*	9	1	3
14	4–5	10	3
15	4	10	4
17	5	3	3
18	7	1–2	3
20	4–5	2	3
21	4–5	2	5
22	4	2	4
26(R=H)	5	2	7

[1] D too weak.

* With 0.025 g. of the sensitizing compound.

EXAMPLE 5

Photosensitive compositions of 250 mg. of carbon tetrabromide, 200 mg. of iodoform, 30 mg. of di-β-naphthospiropyran (compound 1 of Table 1) and 5 mg. of one of the sensitizing compounds indicated by number in the description were dissolved in 8 ml. of a 5% solution of polystyrene in methylene chloride. These compositions were coated separately at a thickness of 0.1 mm. onto non-subbed polyethylene terephthalate film strips.

The obtained photosensiitve recording layers were dried, and tested on their print-out and optical development sensitivity as described in Example 4. The results of these tests are listed in Table 6.

TABLE 6

Number of the sensitizing agent	Number of the by print-out reproduced wedge steps	Optical development	
		Duration of the image-wise exposure (sec.)	Duration of the overall exposure for D=1 (sec.)
6	14	0.5	30–40
10	9–10	0.8	60–120
18	11–12	0.8	120
19	11–12	1–2	120

EXAMPLE 6

Photosensitive compositions of 250 mg. of carbon tetrabromide, 250 mg. of iodoform, 30 mg. of spiropyran compound No. 1 of Table 1, and 5 mg. of sensitizing agent indicated by number in the description were dissolved in 8 ml. of 5% solution of polystyrene in methylene chloride. These compositions were coated at a thickness of 0.1 mm. onto unsubbed polyethylene terephthalate film strips.

The obtained photosensitive recording layers were dried in the dark.

In order to determine the optical development sensitivity the recording layers were subjected to a relatively short (see Table 7) image-wise exposure with a 300 w.-tungsten incandescent lamp placed at a distance of 10 cm. hereby forming a latent or barely visible image. Subsequently the image-wise exposed recording layers were subjected to an overall exposure (see Table 7) with a 250 w. infra-red lamp (Bie and Berntsen, Copenhagen, Denmark) placed at a distance of 15 cm. and irradiating the recording layers through a cut-off filter which absorbs substantially all the light with wavelength below 580 nm.

Dye images with an optical density (D) of 1 and corresponding with the exposed portions of the recording layers were obtained.

The optically developed recording layers were stabilized (fixed) by heating at 120° C. for 10 min.

TABLE 7

Number of the sensitizing agent	Optical development	
	Duration of the image-wise exposure (sec.)	Duration of the overall exposure for D=1 (sec.)
6	1	45
10	2	300
18	2	60
19	2	180
20	2	240
24	1	60–120

EXAMPLE 7

A photosensitive composition consisting of 200 mg. of carbon tetrabromide, 200 mg. of iodoform, 10 mg. of spiropyran compound no. 1 of Table 1, 5 mg. of Michler's ketone and 8 ml. of a 5% solution of polystyrene in methylene chloride was coated at a thickness of 0.1 mm. onto an unsubbed polyethylene terephthalate support and dried.

A contact exposure through a continuous tone black-and-white negative transparency yielded an excellent print-out copy having opposite image values with respect to the original. The exposure lasted 2 min. and was carried out with a HP lamp-80 w. (trade name) placed at a distance of 10 cm.

EXAMPLE 8

250 mg. of carbon tetrabromide, 250 mg. of iodoform, 5 mg. of Michler's ketone, and 30 mg. of 2(o-hydroxy naphthavinyl)-β-naphthopyrilium bromide were dissolved in 8 ml. of a 5% solution of polystyrene in methylene chloride. The addition of some traces of water did almost completely decolourize the obtained solution.

After coating onto an unsubbed polyethylene terephthalate film and drying a completely colourless layer was obtained. Said layer possessed the same recording properties as the recording layer of sample D described in Example 1.

The images obtained with such recording layer were completely stable against fading by light after fixation (heat-treatment at 120° C.).

EXAMPLE 9

500 mg. of carbon tetrabromide, 10 mg. of 2(o-hydroxy naphthavinyl)-β-naphthopyrilium chloride, 1 mg. of Michler's ketone and 8 ml. of a 5% solution of polystyrene in methylene chloride were coated at a thickness of 0.1 mm. onto an unsubbed polyethylene terephthalate support.

After drying a practically completely colorless recording layer was obtained.

An image-wise contact exposure lasting 6 sec. effected through a line image transparency by means of a HP-lamp-80 w. (trade name) placed at a distance of 10 cm. was sufficient to effect an optical development with an infra-red lamp and a cut-off filter (Corning filter CS 3–67) so that in correspondence with the image-wise exposed areas of the recording layer a very dense cyan colored dye image was obtained.

After a fixation of 10 min. at 120° C. an image being perfectly stable against bleaching was obtained.

EXAMPLE 10

A photosensitive composition of 500 mg. of carbon tetrabromide, 150 mg. of iodoform, 20 mg. of spiropyran compound No. 1 of Table 1, 5 mg. of 2,6-ditert.butyl-p-cresol, 2 mg. of the sensitizing agent No. 24 dissolved in 8 ml. of a 5% solution of polystyrene in methylene chloride was coated at a thickness of 0.1 mm. onto a non-subbed polyethylene terephthalate film support.

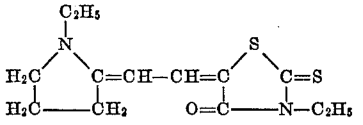
The dried recording layer was in contact with an opaque line original (printed text on paper) exposed reflectographically for 1 second using as exposure source a 300 w. incandescent tungsten lamp placed at a distance of 10 cm. from the recording layer.

The optical development was effected by means of an overall exposure carried out with a 250 w.-infrared lamp (Bie and Berntsen, Copenhagen, Denmark) using a cut-off filter absorbing substantially all the light with a wavelength smaller than 540 nm.

A practically fog-free optically sufficiently dense negative image of the original was obtained.

EXAMPLE 11

A photosensitive composition consisting of 200 mg. of carbon tetrabromide, 200 mg. of iodoform, 40 mg. of dinaphthospiropyran, 20 mg. of triphenylstibine, 10 mg. of 2-mercapto-benzthiazole, 0.003 g. of a merocyanine dye having the following structure:



and 8 ml. of a 5% by weight solution of poly-N-vinylcarbazole in methylene chloride was coated at a thickness of 0.12 mm. onto a non-subbed polyethylene terephthalate support. The coated layer was dried for 30 min. at 50° C.

The obtained photosensitive recording layer was contact-exposed for 1 sec. through a transparent line original. The exposure was carried out with a 3M Photocopier 179 (trade name) operating with a white light exposure source (setting ½). A latent image was formed which was developed optically by means of an overall exposure through a cut-off filter absorbing all the light having a wavelength smaller than 540 nm. and using a 250 w. infra-red lamp placed at a distance of 15 cm. On effecting that overall exposure whilst keeping the recording material in thermal contact with a hot plate (60° C.) the optical development proceeded within less than 2 sec. reaching an image density of more than 2.5 (measured in transmission).

The fixation of the obtained visible image proceeded by heating the recording material at 175° C. for 10 sec. under strong air circulation.

In the absence of 2-mercapto-benzthiazole or without applying heat during the optical development the formation of the visible image was markedly slower.

EXAMPLE 12

A photosensitive composition consisting of 100 mg. of iodoform, 50 mg. of 3-phenyl-di-β-naphthospiropyran, 5 mg. of Michler's ketone and 4 ml. of a 5% solution in a butanone/methylene chloride (⅓ by volume) of a phenoxy-polymer prepared from 2,2′-bis(4-hydroxyphenyl)propane and 1-chloro-2,3-epoxypropane was coated at a thickness of 0.12 mm. onto a non-subbed polyethylene terephthalate film.

After drying the coating was exposed for 2 minutes through a step wedge having a density increment of 0.15 using a 80 w. high pressure mercury vapor bulb, type HPL of N.V. Philips' Gloeilampenfabrieken, Eindhoven (The Netherlands) placed at a distance of 10 cm.

After a stabilization treatment for 3 min. at 120° C. a green print-out wedge image containing 7 reproduced steps was obtained.

In the following table the results obtained with different spiropyran compounds listed in the description by number are indicated.

TABLE

Number of the spiropyran compound	Number of the by print-out reproduced steps	Color of the image
31	8	Red.
32	6	Yellow.
34	6	Blue.
35	6	Do.
36	5	Yellow.
38	8	Dark blue.
39	7	Do.

EXAMPLE 13

A photosensitive composition consisting of 100 mg. of carbon tetrabromide, 100 mg. of iodoform, 100 mg. of 3-methyl-di-β-naphthospiropyran, 10 mg. of Michler's ketone and 10 ml. of a 5% solution of polystyrene in methylene chloride was coated at a thickness of 0.1 mm. onto an unsubbed polyethylene terephthalate film.

The obtained photosensitive recording layer was dried at 60° C.

The electron-beam sensitivity of the photosensitive layer was tested in a vacuum of 10^{-4} mm. Hg.

The electron beam recording proceeded with electrons accelerated by a potential difference of 20 kv. The charge density measured at the level of the recording layer was 2.10^{-6} coulomb per sq. cm.

The optical density (measured in transmittance) of the area struck by the electron beam was 0.5. The measurement was preceded by a thermal stabilization at 150° C.

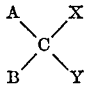
We claim:

1. A photographic process for forming a visible image in a recording material which comprises in intimate admixture:

(1) at least one spiropyran compound of the group consisting of spirodibenzopyran, a spirodinaphthopyran, a 1,3,3-trimethylindolino-benzospiropyran, a 1,3,3-trimethylindolinonaphthospiropyran, or a spiropyran that contains a condensed anthracene or phenanthrene nucleus;

(2) at least one ultra-violet light-sensitive organic polyhalogen compound capable of producing on exposure with ultra-violet light a dye salt with the

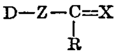
spiropyran compound and having the general formula:



wherein:

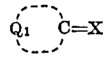
- each of A, B, X and Y is a chlorine, bromine or iodine; or
- one of said radicals A, B, X or Y is an alkyl group, an aryl group or an aroyl group and the other radicals are each chlorine, bromine or iodine; or two of said radicals A, B, X or Y each is an aromatic acyl group and the other radicals are each chlorine, bromine or iodine; and

(3) in working relationship with said mixture (A) an organic compound containing two radicals of different electron-affinity linked to each other through a conjugated system, and having one of the following general Formulae (I), (II), (III), (IV), (V) or (VI):

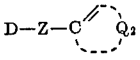


$D-Z-\underset{R}{\underset{|}{C}}=X$ (I)

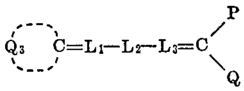
$D-Z-Y-Z-D$ (II)



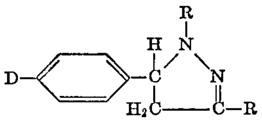
(III)



(IV)



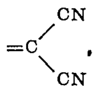
(V)



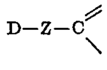
(VI)

wherein:

- D represents an electron-donating group selected from an amino group substituted with alkyl, cycloalkyl or aralkyl, a hydroxy group or a hydroxy group substituted with alkyl, cycloalkyl or aralkyl,
- Z represents a polymethine chain, an azamethine chain, phenylene or naphthalene,
- R represents hydrogen, an alkyl group, an aryl group or the necessary atoms to form a homocyclic ring with an atom of the group Z,
- Q_1 represents the non-metal atoms necessary to complete a ring or ring system in which the group C=X is linked through a conjugated system of methine groups or of a chain of methine groups bound to nitrogen to a group D,
- X represents an electronegative atom or group being selected from the group consisting of oxygen, =N—R wherein R is hydrogen or an aromatic group, sulphur, selenium, or

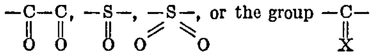


- Q_2 represents the necessary atoms to form with the carbon atom of the group



a heterocyclic ring having an electro negative character with respect to the group D,

- Y represents an electron-attracting group selected from the group consisting of

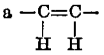


$-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}$, $-\underset{\underset{O}{\|}}{S}-$, $-S(=O)_2-$, or the group $-\underset{\underset{X}{\|}}{C}-$,

wherein X has the above meaning,

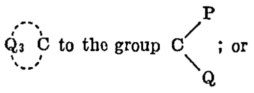
- Q_3 represents a heterocyclic nucleus, containing an alkylamino group,
- P and Q each represent an electron-attracting cyano group, or P and Q together represent the necessary atoms to close a heterocyclic ring with electronegative character,

each of L_1 and L_3 represent a methine group, and L_2 represents a monovalent chemical bond,



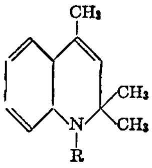
a $-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-$

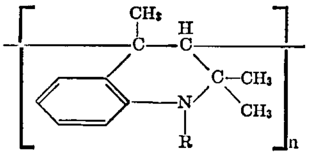
group or a plurality of such group linked to each other, or L_1, L_2 and L_3 represent together a double bond linking the group



or

(B) organic compounds containing an aromatic ring having two adjacent carbon atoms thereof in common with an adjacent ring free of conjugation, said adjacent ring at one end being linked to said aromatic ring through a carbon-carbon bond and at the other end is linked to said ring through an electron-donating group and having one of the following structural formulae:





wherein:

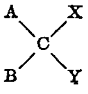
n is a positive integer of at least 2, and
R is hydrogen or an alkyl group,

said process comprising the steps of exposing said recording material to activating electromagnetic radiation of an intensity sufficient to produce a visible image directly or a latent image that can be rendered visible by optical development.

2. A photosensitive recording material for the direct production of a visible image by imagewise exposure to activating electromagnetic radiation which comprises a layer of an intimate mixture consisting essentially of:

(1) at least one spiropyran compound of the group consisting of a spirodibenzopyran, a spirodinaphthopyran, a spirobenzonaphthopyran, a 1,3,3-trimethylindolino-benzospiropyran, a 1,3,3-trimethylindolinonaphthospiropyran, or a spiropyran that contains a condensed anthracene or phenanthrene nucleus;

(2) at least one ultra-violet light-sensitive organic polyhalogen compound capable of producing on exposure with ultra-violet light a dye salt with the spiropyran compound and having the general formula:

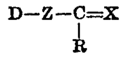


wherein:

each of A, B, X and Y is a chlorine, bromine or iodine atom; or

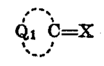
one of said radicals A, B, X or Y is an alkyl group, an aryl group, or an aroyl group and the other radicals are each chlorine, bromine or iodine; or two of said radicals A, B, X or Y each is an aromatic acyl group and the other radicals are each chlorine, bromine or iodine; and

(3) in working relationship with said mixture (A) an organic compound containing two radicals of different electron-affinity linked to each other through a conjugated system, and having one of the following general formulae (I), (II), (III), (IV), (V) or (VI):

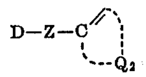


$$\underset{\displaystyle R}{\mathrm{D-Z-C{=}X}} \qquad \text{(I)}$$

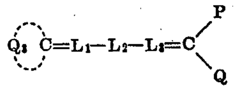
$$\mathrm{D-Z-Y-Z-D} \qquad \text{(II)}$$



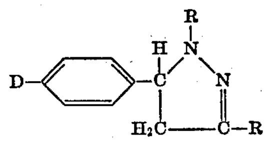
(III)



(IV)



(V)



(VI)

wherein:

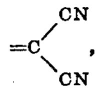
D represents an electron-donating group selected from an amino group substituted with alkyl, cycloalkyl or aralkyl, a hydroxy group or a hydroxy group substituted with alkyl, cycloalkyl or aralkyl,

Z represents a polymethine chain, an azamethine chain, phenylene or naphthalene,

R represents hydrogen, an alkyl group, an aryl group or the necessary atoms to form a homocyclic or heterocyclic ring with an atom of the group Z,

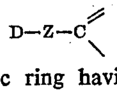
Q_1 represents the non-metal atoms necessary to complete a ring or ring system in which the group C=X is linked through a conjugated system of methine groups or of a chain of methine groups bound to nitrogen to a group D,

X represents an electronegative atom or group being selected from the group consisting of oxygen, =N—R wherein R is hydrogen or an aromatic group, sulphur, selenium, or



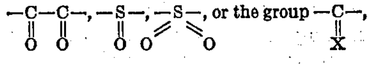
$$=\mathrm{C(CN)_2},$$

Q_2 represents the necessary atoms to form with the carbon atom of the group



a heterocyclic ring having an electronegative character with respect to the group D,

Y represents an electron-attracting group selected from the group consisting of



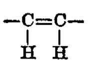
$$-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-\underset{\displaystyle O}{\underset{\|}{C}}-,\ -\underset{\displaystyle O}{\underset{\|}{S}}-,\ -\mathrm{S}(=\mathrm{O})_2-,\ \text{or the group } -\underset{\displaystyle X}{\underset{\|}{C}}-,$$

wherein X has the above meaning,

Q_3 represents a heterocyclic nucleus, containing an alkylamino group,

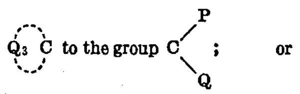
P and Q each represent an electron-attracting cyano group, or P and Q together represent the necessary atoms to close a heterocyclic ring with electronegative character,

each of L_1 and L_3 represent a methine group, and L_2 represents a monovalent chemical bond, a



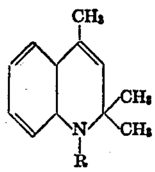
$$-\underset{\displaystyle H}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-$$

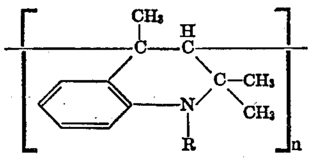
group or a plurality of such group linked to each other, or L_1, L_2 and L_3 represent together a double bond linking the group



; or

(B) organic compounds containing an aromatic ring having two adjacent carbon atoms thereof in common with an adjacent ring free of conjugation, said adjacent ring at one end being linked to said aromatic ring through a carbon-carbon bond and at the other end is linked to said ring through an electron-donating group and having one of the following structural formulae:





wherein:

n is a positive integer of at least 2, and

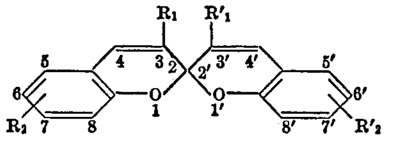
R is hydrogen or an alkyl group.

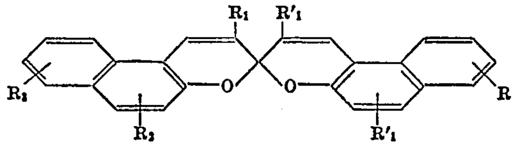
3. The process of claim **1** wherein said exposure produces a latent image and said latent image is optically developed and comprising the steps of: imagewise exposing the recording material to activating electromagnetic radiation of an intensity sufficient to bring about a latent or barely visible image having an increased spectral sensitivity in a wavelength range outside the inherent sensitivity range of the ultra-violet light-sensitive compound, and then uniformly exposing the entire imagewise exposed recording material to light within the wavelength range for which the initially exposed portions are of increased sensitivity than the initially non-exposed portions, thereby increasing the visibility of said initially formed range.

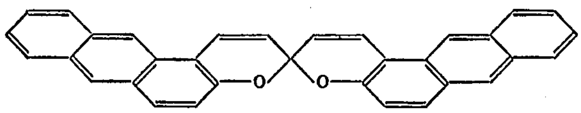
4. The process of claim **1** wherein said exposure produces a latent image and said latent image is optically developed and comprising the steps of: uniformly exposing the entire recording material to electromagnetic radiation of an intensity sufficient to bring about in the recording material an increase in its spectral sensitivity in a wavelength range outside the inherent sensitivity range of the ultra-violet light-sensitive compound, and then imagewise exposing the overall exposed recording material within the wavelength range for which the overall exposed recording material is of increased sensitivity to increase the visibility of the initially formed image.

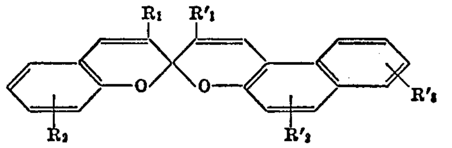
5. A photographic process according to claim **1** wherein the recording material after the formation of a visible image is overall heated to bring about image stabilization.

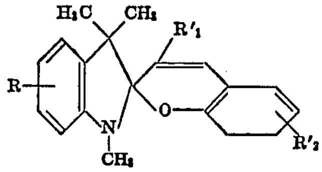
6. A photographic process according to claim **1** wherein said spiropyran compound corresponds to one of the following general formulae:

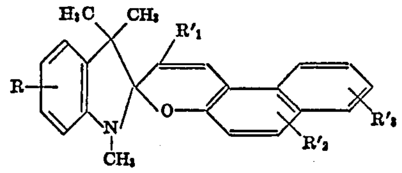


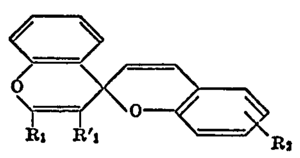












wherein: R, R_1, R'_1, R_2, R'_2, R_3 and R'_3 each represent hydrogen, alkyl, alkyl substituted with halogen, alkyl substituted with an ester group, alkyl substituted with a carboxyl group, alkyl substituted with a N-phenylcarbamyl group, a hydroxy group, an alkoxy group, an aryloxy group, a phenyl group, piperidyl, acetyl, halogen, nitro, or R_1 and R'_1 together represent a —$(CH_2)_n$-chain wherein $n=2$ or 3 to link the carbon atoms in the 3 and 3′ positions together.

7. A process according to claim **1** wherein said ultraviolet light-sensitive compound is carbon tetrabromide or iodoform or a mixture thereof.

8. A process according to claim **1** wherein said recording material contains as an anti-fogging agent a triaryl compound of a group V element or a sterically hindered phenol.

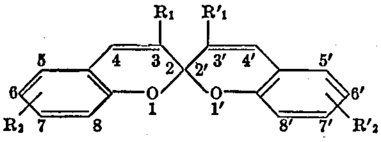
9. A process according to claim **1** wherein the mixture is present in a layer of at least one polymeric binding agent of the group of styrene, vinyl acetate, acrylonitrile, acrylic acid ester, methacrylic acid ester, N-vinylcarbazole or butadiene units, a hydrophobic cellulose derivative, a phenoxy resin or polyester polycondensate.

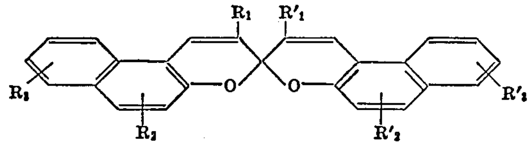
10. A process according to claim **1** wherein the exposure is a direct exposure.

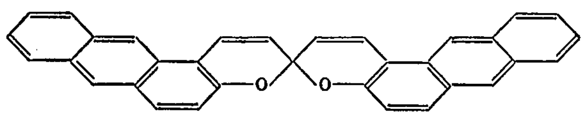
11. A process according to claim **1** wherein the exposure is a reflex exposure.

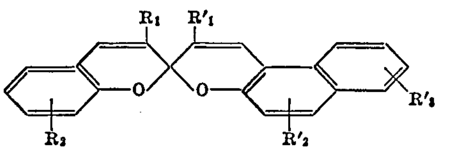
12. A process according to claim **1** wherein the exposure is an electron beam exposure.

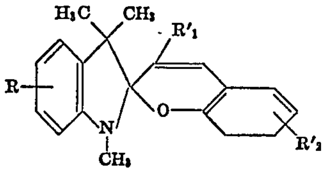
13. A photographic material according to claim **2** wherein said spiropyran compound corresponds to one of the following general formulae:

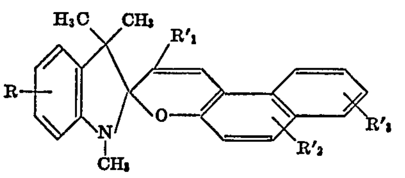


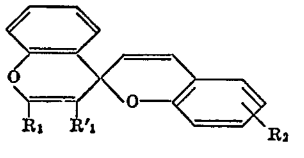












wherein: R, R_1, R'_1, R_2, R'_2, R_3 and R'_3 each represent hydrogen, alkyl, alkyl substituted with halogen, alkyl substituted with an ester group, alkyl substituted with a carboxyl group, alkyl substituted with a N-phenylcarbamyl group, a hydroxy group, an alkoxy group, an aryloxy group, a phenyl group, piperidyl, acetyl, halogen, nitro, or R_1 and R'_1 together represent a —$(CH_2)_n$-chain wherein $n=2$ or 3 to link the carbon atoms in the 3 and 3′ positions together.

14. A material according to claim **2** wherein said ultraviolet light-sensitive compound is carbon tetrabromide or iodoform or a mixture thereof.

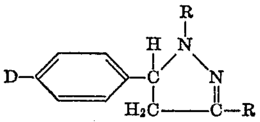
15. A photosensitive recording material according to claim **2**, containing as an anti-fogging agent a triaryl compound of a group V element and a sterically hindered phenol.

16. A photosensitive recording material according to claim **2**, wherein the recording material contains said spiropyran compound in admixture with said photosensitive organic polyhalogen compound in a ratio by weight of 1:1–50.

17. A photosensitive recording material according to claim **16** wherein the recording material contains triphenyl stilbine with respect to said photosensitive polyhalogen compound in a ratio by weight in the range of 1:100 to 2.5:100.

18. The material according to claim **17** wherein said compound 3 is a merocyanine dye or a styryl dye base.

19. The material according to claim **17** wherein said compound 3 has the structural formula:



wherein:

D is an electron-donating group, and
R is hydrogen or a linear or homocyclic hydrocarbon radical.

20. The process as in claim **1** wherein said compound 3 is present in a ratio by weight relative to said spiropyran compound 1 of up to about ½.

21. The material as in claim **2** wherein said compound 3 is present in a ratio by weight relative to said spiropyran compound 1 of up to about ½.

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U.S. Cl. X.R.

96—90 PC, 90 R, 48 QP; 250—323

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,813,245 Dated May 28, 1974

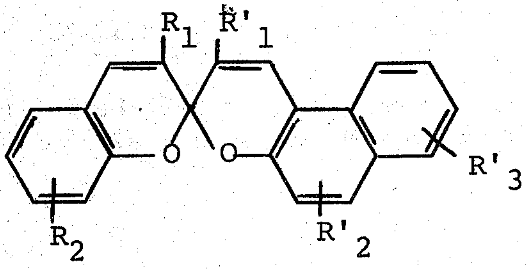
Inventor(s) Urbain Leopold LARIDON et al

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

Column 30, Claim 1, line 69, before "a 1,3,3-", insert -- a spirobenzonaphthopyran, --.

Column 31, Claim 1, line 9, after "iodine", insert -- atom --.
line 54, , after "cyclic", insert -- or heterocyclic --.

Column 36, Claim 13, fourth formula should read --



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Signed and sealed this 15th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents