

[54] **THERMOIMAGING PROCESS UTILIZING A PHOTOCHROMIC MATERIAL CONTAINING A SPIROPYRAN, A POLYHALOGENATED HYDROCARBON, A THIOL COMPOUND AND A POLYVINYLCARBAZOLE**

[75] Inventors: **Jozef Willy Van den Houte**, Berchem; **Freddy Ghisleen Van Royen**, Wommelgem; **Hugo Vital Van Goethem**, Edegem; **Edwin Hendrik Hazenbosch**, Mechelen, all of Belgium

[73] Assignee: **Agfa-Gevaert**, Mortsels, Belgium

[22] Filed: **June 25, 1973**

[21] Appl. No.: **372,938**

[30] **Foreign Application Priority Data**

June 26, 1972 United Kingdom..... 29915/72

[52] U.S. Cl..... **250/316**; 96/27 R; 96/48 R; 96/48 QP; 96/90 R; 96/90 PC

[51] Int. Cl. .... **G03c 5/04**; G03c 1/52

[58] Field of Search.... 96/27 R, 48 R, 48 QP, 90 R, 96/90 PC; 250/316, 317

[56] **References Cited**

**UNITED STATES PATENTS**

3,359,105	12/1967	Wainer .....	96/90
3,451,338	6/1969	Baum.....	96/90 PC
3,642,479	2/1972	Van Allen et al. ....	96/90 PC

3,785,820	1/1974	Inoue, et al. ....	96/90 PC
3,810,762	5/1974	Laridon et al. ....	96/90 R
3,820,995	6/1974	Mertens et al. ....	96/90 R

**FOREIGN PATENTS OR APPLICATIONS**

1,274,655	8/1968	Germany .....	96/90 PC
-----------	--------	---------------	----------

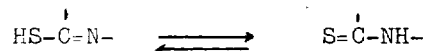
Primary Examiner—**Won H. Louie, Jr.**

Attorney, Agent, or Firm—**William J. Daniel**

[57] **ABSTRACT**

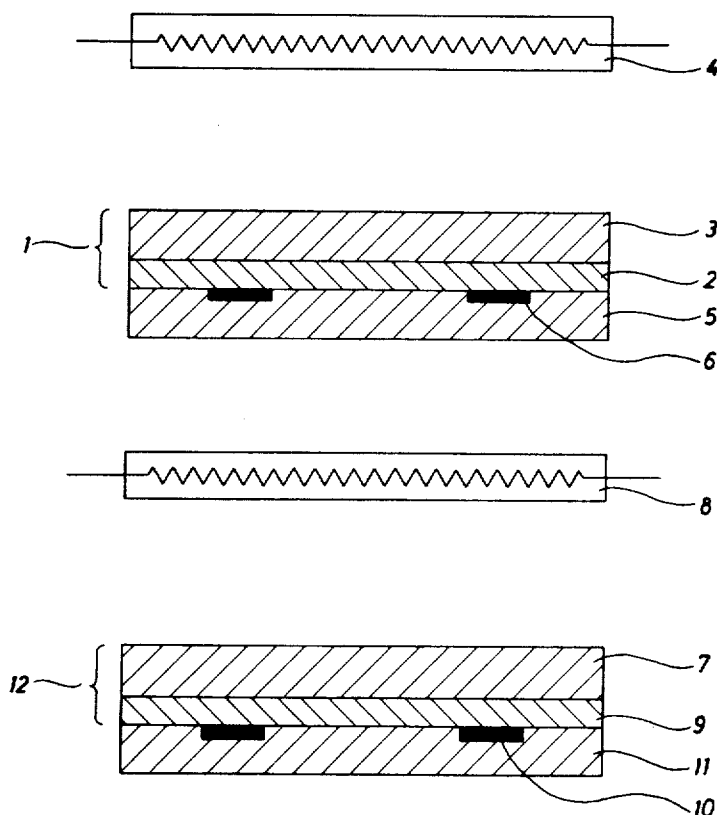
A process for forming a dye image comprising the image-wise heating in the presence of minor amounts of visible light of a recording material containing an intimate mixture comprising:

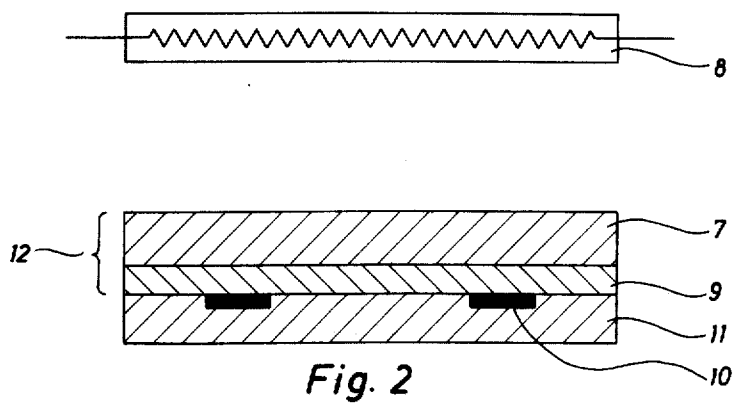
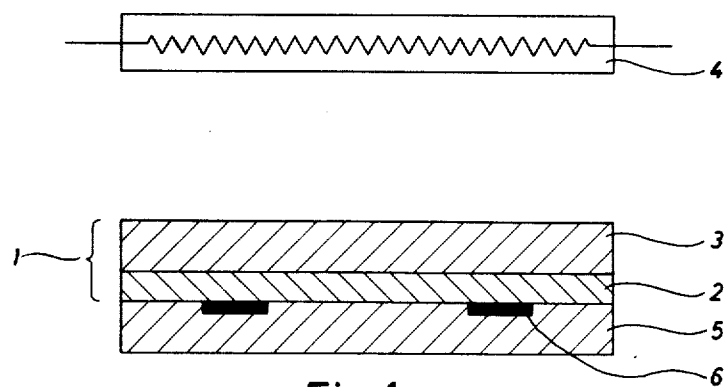
1. at least one spiropyran compound,
2. at least one ultraviolet-radiation sensitive compound capable of producing on exposure to ultraviolet-radiation with the spiropyran compound a dye salt, and in working relationship with said mixture a compound or mixture of compounds belonging to one of the following classes.
  - a. an organic nitrogen-containing compound comprising a thiol group or in its tautomeric form a thione group as represented in the following tautomeric structural parts:



- b. a polymer containing N-vinylcarbazole units.

**15 Claims, 2 Drawing Figures**

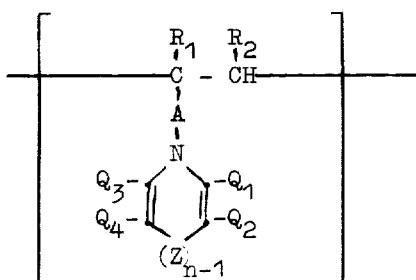




**THERMOIMAGING PROCESS UTILIZING A  
PHOTOCHROMIC MATERIAL CONTAINING A  
SPIROPYRAN, A POLYHALOGENATED  
HYDROCARBON, A THIOL COMPOUND AND A  
POLYVINYL CARBAZOLE**

This invention relates to thermographic recording.  
The Belgian Pat. No. 771,848 relates to a photographic process, wherein a recording material, containing an intimate mixture comprising

1. at least one spiropyran compound,
2. at least one ultra-violet-sensitive compound capable of producing on exposure to ultra-violet radiation with the spiropyran compound a dye salt, and in working relationship with said mixture one or more compounds belonging to one of the following classes:
  - A. polycyclic aromatic compounds,
  - B. aromatic carbonyl compounds,
  - C. organic compounds containing two radicals of different electron-affinity, the term radical including group and atom, linked to each other through a conjugated system,
  - D. 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 that has no conjugated character and at one end is linked to the aromatic nucleus or ring system through a carbon-carbon bond and at the other end linked to said nucleus or ring system through an electron-donating group, said organic compounds including those having a said nucleus or ring system in substituted form,
  - E. polymeric compounds containing recurring units of the following general formula:



wherein:

- Z represents sulphur or a single bond,  
A represents a single bond or a divalent hydrocarbon group,  
each of  $R_1$  and  $R_2$  represents hydrogen or a lower alkyl radical,  
each of  $Q_1$  and  $Q_2$  represents hydrogen or together represent the necessary atoms to close an adjacent carbocyclic nucleus including a substituted adjacent carbocyclic nucleus,  
each of  $Q_3$  and  $Q_4$  represents hydrogen or together represent the necessary atoms to close an adjacent carbocyclic nucleus including a substituted adjacent carbocyclic nucleus, and  $n$  represents 1 or 2.
- F. organic nitrogen-containing compounds having a thiol group or in their tautomeric form a thione

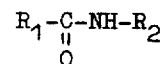
group as represented in the following tautomeric structural parts:



G. inorganic compounds producing photoelectrons under the influence of activating electromagnetic radiation and having a basic or amphoteric character,

exposed information-wise to activating electromagnetic radiation of a dose being sufficient to bring about a directly visible image.

- The United Kingdom Patent Application No. 40,349/71 being a modification of the United Kingdom Patent Application No. 41,749/70, which corresponds with the above-mentioned Belgian Pat. No. 771,848 relates to the use of an amido, acylamino or ureido compound in a photographic process operating with said spiropyran and ultraviolet-sensitive compound. The amido, acylamino, or ureido compound used in admixture with said spiropyran compound and ultraviolet-sensitive compound corresponds to the following general formula:



wherein:

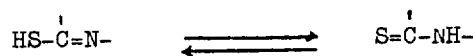
$R_1$  represents an organic group, e.g. of the type present in a carboxylic acid chloride, e.g. an alkyl group, an aryl group, or heterocyclic group including these groups in substituted form, or a  $-NHR_3$  or



group, in which each of  $R_3$  and  $R_4$  represents an alkyl group or an aryl group, e.g. a phenyl group including these groups in substituted form, and

- $R_2$  represents hydrogen or an organic group as is directly linked to the  $-NH_2$  group of an organic amino compound, e.g. an alkyl group, an aryl group, or a heterocyclic group including these groups in substituted form.

It has now been found that recording materials described in the above mentioned United Kingdom Patent Application No. 40,349/71 and in the Belgian Pat. No. 771,848 having in the recording layer composition an organic nitrogen-containing compound comprising a thiol group or in its tautomeric form a thione group as represented in the following tautomeric structural parts:



and/or having in that composition a polymer containing N-vinylcarbazole units, preferably poly-N-vinylcarbazole, are suited for visible image formation in a thermographic recording process in which the information-wise heating takes place in the presence of minor amounts of visible light.

According to a preferred recording embodiment of the present invention the recording material is exposed with infrared radiation and a minor amount of visible light while being in heat-conductive contact with an original containing infrared-absorbing image markings. The exposure is preferably reflectographical i.e. the infrared radiation is allowed to pass first through the recording material before it strikes the original. According to this embodiment the infrared-absorbing image markings of the original are heated and the heat generated in these markings is transmitted by conduction to the recording layer. The infrared-absorbing image markings are, e.g., printed characters the ink of which contains carbon black or a metallic compound.

Two possible ways of effecting reflectographic exposure are illustrated in the accompanying FIG. 1 and FIG. 2.

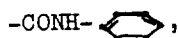
According to the reflectographic exposure technique of FIG. 1 a photosensitive material 1 comprising a photo-sensitive layer 2 applied to a support 3, which is capable of transmitting infrared radiation and visible light is placed between the infrared radiation source 4 and the original 5 bearing infra-red-absorbing indicia 6, during the exposure.

According to the reflectographic exposure technique of FIG. 2 the photosensitive layer 7 of the photosensitive material 12 is facing the infrared radiation source 8. During exposure the support 9 of the photosensitive layer 7 is in contact with the infrared-absorbing indicia 10 of the original 11. The support 9 of the photosensitive layer 7 is thin and heat-conducting. In both exposure arrangements the infrared exposure source emits infra-red radiation and a minor amount, e.g. up to 20 percent of visible light.

Spiropyran compounds suited for photo-thermographic 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 form, e.g. an anthraceno or a phenanthreno ring system as is present e.g. in a spirodibenzopyran, a spirodinaphthopyran, a spirobenzonaphthopyran, a 1,3,3-trimethylindolinobenzospiropyran, a 1,3,3-trimethyl-indolinonaphthospiropyran or such spiropyran containing condensed aromatic nuclei of the anthracene or phenanthrene type.

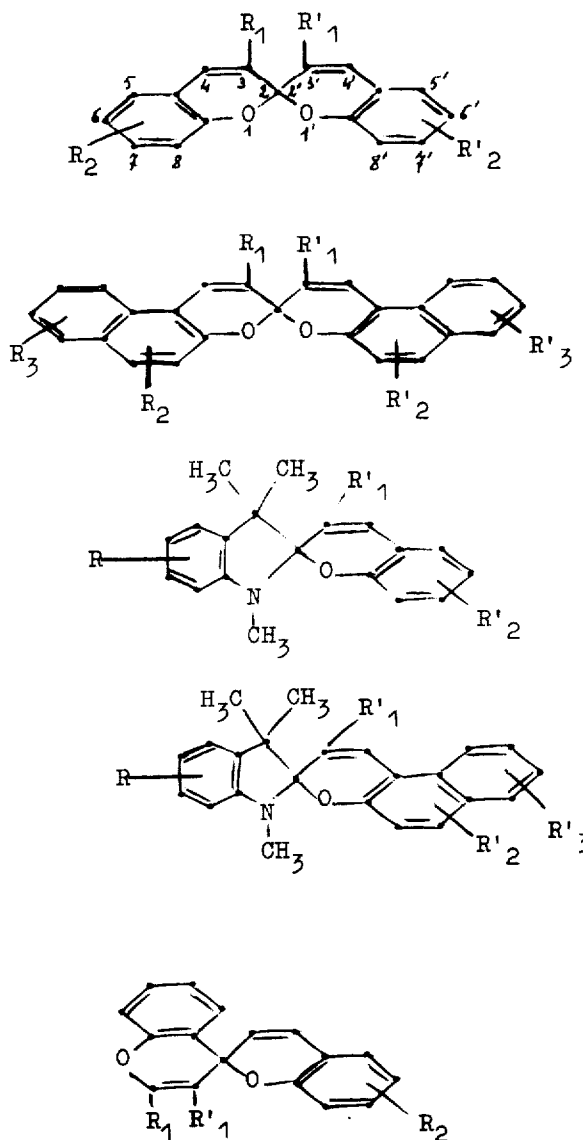
In said spiropyran the pyran rings, the condensed benzo, the condensed higher aromatic rings as well as the 1,3,3-trimethylindolino ring may be substituted.

Suitable substituents therefor are, e.g., hydrocarbon groups such as alkyl groups, e.g. lower alkyl groups such as methyl, substituted alkyl groups, e.g. substituted with halogen, or phenyl-substituted alkyl groups, alkylene ester groups e.g.  $-\text{CH}_2-\text{COOC}_2\text{H}_5$ , alkylene carboxyl groups e.g.  $-\text{CH}_2-\text{COOH}$ , carbonamide groups or substituted carbonamide groups e.g.



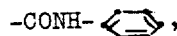
halogen, nitro, hydroxy, alkoxy, aryloxy or a substituent linking the carbon atoms in 3,3'-position in the spiropyran system together, e.g. a  $(\text{CH}_2)_n$ -chain wherein  $n$  is 2 or 3.

General formulae covering particularly suited spiropyran are the following:



wherein:

each of  $R$ ,  $R_1$ ,  $R'_1$ ,  $R_2$ ,  $R'_2$ ,  $R_3$ , and  $R'_3$  represents hydrogen, an aliphatic group including a substituted aliphatic group, e.g. a  $(\text{C}_1-\text{C}_{20})$  alkyl group including such an alkyl group in substituted form, more particularly methyl, ethyl, propyl, amyl or hexadecyl or a 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.  $-\text{CH}_2-\text{COOC}_2\text{H}_5$ , an alkylene carboxyl group, e.g.  $-\text{CH}_2-\text{COOH}$ , a carbonamide group or a substituted carbonamide group, e.g.



or  $R_1$  and  $R'_1$  together represent a  $-(\text{CH}_2)_n-$  chain wherein  $n=2$ , or 3 to link the carbon atoms in the 3 and 3' positions together.

Suitable spiropyran compounds and their preparation are described in the published German Pat. Nos. 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. Diltthey, Berres, Holterkoff, Wubken, J. Prakt. Chem. [2] 114, 187 (1926), by C. F. Koelsch and W. R. Workman in J. Am. Chem. Soc. 74 6288 (1952) and

by I. M. Heilbron and G. F. Howard in J. Chem. Soc. (1934), 1571.

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

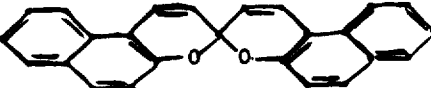
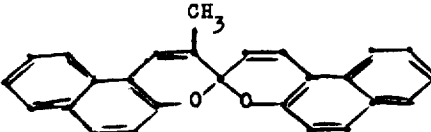
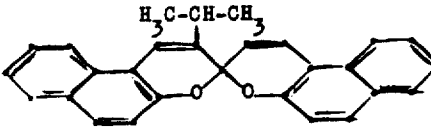
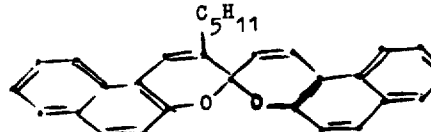
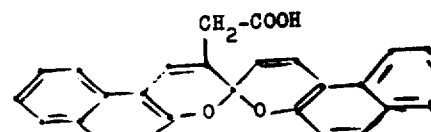
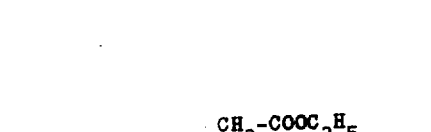
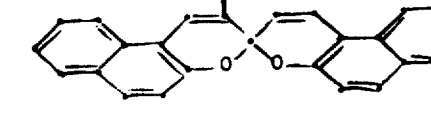
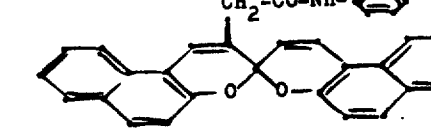
Spiropyran compound	Melting point (°C)
1. 	257
2. 	204
3. 	208
4. 	185
5. 	164
6. 	166
7. 	210
8. 	238



Table I—Continued

Spiropyran compound	Melting point (°C)
19.	185
20.	206
21.	180
22.	88
23.	> 260
24.	173
25.	193
26.	158

Table 1-Continued

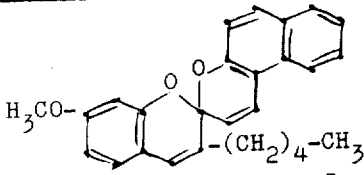
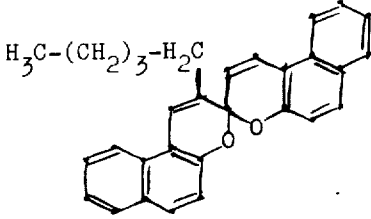
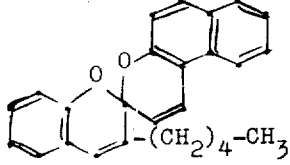
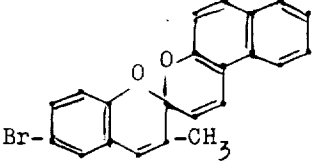
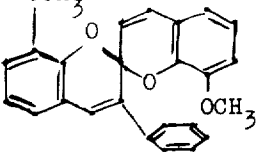
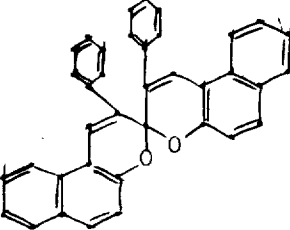
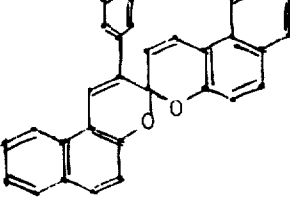
Spiropyran compound	Melting point (°C)
27. 	144
28. 	180
29. 	160
30. 	112
31. 	120
32. 	± 200
33. 	248



Table 1 - Continued

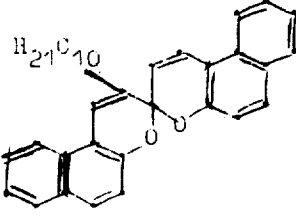
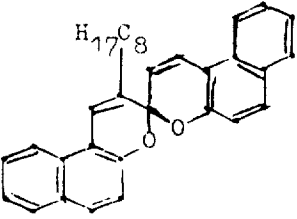
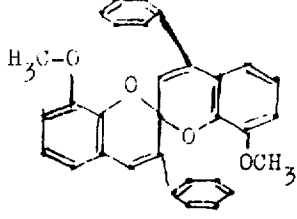
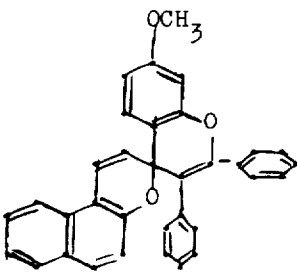
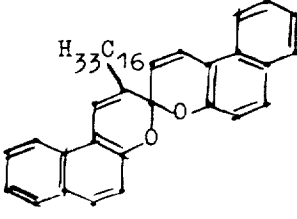
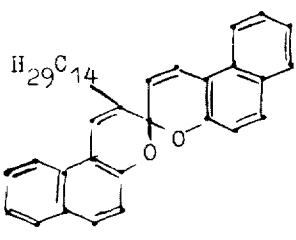
Spiropyran compound	Melting point (°C)
34. 	152
35. 	160
36. 	± 250
37. 	173
38. 	133

Table 1—Continued

Spiropyran compound	Melting point (°C)
39. 	146

In order to illustrate the preparation of the diarylospiro-  
pyran and the indolino-arylospiropyran com-  
pounds, more detailedly, the following preparations are  
given:

#### PREPARATION 1

##### Preparation of 3-methyldi- $\beta$ -naphthospiropyran (compound 2 of Table 1)

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

ethanol	1 litre
butanone	22 ml (0.25 mole)
2-hydroxy-1-naphthaldehyde	86 g (0.5 mole)

The flask is shaken until partial dissolution of the in-  
gredients. Dry hydrogen chloride gas is introduced at  
a rate, which allows complete absorption and the start  
of ethanol reflux. Thereupon the already highly blue  
mixture is cooled in a mixture of ice and sodium chlo-  
ride and the introduction of hydrogen chloride gas con-  
tinued until saturation. In the reaction mixture green  
crystals of pyrylium salt are formed and the crystalliza-  
tion is allowed to proceed overnight in a refrigerator.

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

A 10 percent by weight aqueous solution of ammo-  
nium hydroxide is added with stirring until the mixture  
is definitely alkaline. During this operation the mixture  
becomes colourless.

The obtained crystalline product is separated by suc-  
tion, 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. Melt-  
ing point: 204°C.

#### PREPARATION 2

##### Preparation of 1,3,3-trimethylindolinobenzopyrylospiran (compound 22 of Table 1)

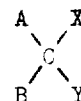
In a 100 ml flask fitted with a reflux condenser the  
following ingredients are introduced:

salicylaldehyde	3.7 g (0.03 mole)
1,3,3-trimethyl-2-methylene indolenine	5.1 g (0.03 mole)
ethanol	90 ml

The solution is refluxed for 2 h. Thereupon the mix-  
ture is cooled and filtered. To the filtrate water is added  
so that a solid product precipitates, which 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, for use according to the present invention is  
preferably an organic polyhalogen compound, from  
which a halogen-containing radical can be separated  
photolytically. Compounds possessing that property  
are within the scope of the following general formula:



wherein:

each of A, B, X, and Y is a halogen atom of the group  
of chlorine, bromine or iodine, or

wherein one of said symbols A, B, X, or Y represents  
an alkyl group, including a substituted alkyl group,  
e.g. a halogen-substituted alkyl group, a hydroxyl-  
alkyl group or an aralkyl group e.g. benzyl, an aryl  
group, a substituted aryl group, or a heterocyclic  
group, e.g. a quinoxaline or quinaldine group or an  
aroyl group and the other symbols are chlorine,  
bromine or iodine, or wherein at least two of said  
symbols A, B, X or Y represent an aromatic acyl  
group e.g. benzoyl and the other symbols chlorine,  
bromine, or iodine.

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

The recording materials used according to the pres-  
ent invention containing a spirodiarylopyran com-  
pound and said thiol or thione compound in combina-  
tion with poly-N-vinylcarbazole have a remarkably  
high sensitivity to white light and particularly to red  
light when spectrally sensitized with acetanilide or ac-  
etanilide derivatives.

Specific examples of such useful sensitizing agents  
are listed in the following table 2.

Table 2

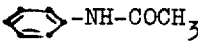



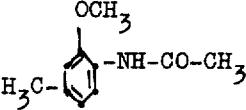
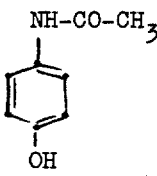


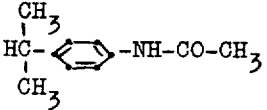


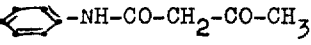
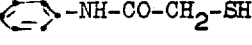
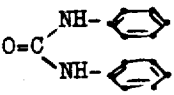
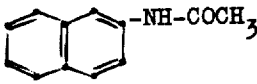
Number of the compound	Structural formula	Melting point °C	Reference for preparation
1	 -NH-CO-CH <sub>3</sub>	150	Ber.60, 219 (1927)
2	H <sub>5</sub> C <sub>2</sub> O-  -NH-CO-CH <sub>3</sub>	135	Arch.der Pharmazie (1926) 324
3	H <sub>3</sub> C-CO-  -NH-CO-CH <sub>3</sub>	166	Rec.Trav. Chim.41,659 (1922)
4	H <sub>3</sub> C-  -NH-CO-CH <sub>3</sub>	147	Monatsh.48, 128
5	 -NH-CO-CH <sub>3</sub>	130	Ber.42,3103 (1909)
6		168	J.Prakt.Chem. [2] 84,530 (1911)
7	H <sub>3</sub> C-CO-NH-  - 	170	Ann.260,234 (1890)
8	 -NH-CO-CH <sub>3</sub>	102	Ber.21,1159 (1888)
9	H <sub>3</sub> C-CO-NH-  -CO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	142	Ber.33,2643 (1900)
10	H <sub>3</sub> C-CO-NH-  -CHO	156	Ber.16,2003 (1883)
11	 -NH-CO-CH <sub>2</sub> -CO-CH <sub>3</sub>	86	Helv.Chim. Acta 11,779
12	 -NH-CO-CH <sub>2</sub> -SH	111	J.Prakt.Chem. [2] 84,649 (1911)

Table 2—Continued

Number of the compound	Structural formula	Melting point °C	Reference for preparation
13		242	A. Vogel, Practical Organic Chemistry, Longmans, Green and Co. Ltd., London, 3rd Ed., p. 646
14		132	J. Chem. Soc. 1926, 8

The amount of spectral sensitizing agent may vary within a wide range depending on the intensity of the effect desired.

Preferred amounts of sensitizing agent are in the weight ratio range of 1:1 to 0.05:1 with respect to the spiropyran compound(s).

Preferred thiol and thione compounds correspond to the following tautomeric structures:



wherein:

X represents oxygen, sulphur, selenium or the group  
-NR

in which R is hydrogen or an organic group, e.g. an alkyl group including a substituted alkyl group, preferably a C<sub>1</sub>-C<sub>5</sub> alkyl group or an aryl 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 benzothiazole, benzoselenazole, benzoxazole or benzimidazole ring.

Particularly useful thiol and thione compounds are listed in the following table 3.

Table 3

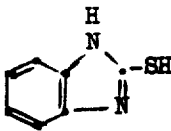
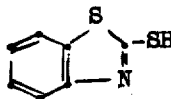
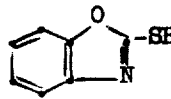
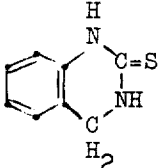
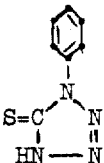
Number of the compound	Structural formula	Melting point °C	Reference for preparation
1		303	Org. Synth. 30, (1950) 56
2			J. Am. Chem. Soc. 49, 1752 (1927)
3		192	Org. Synth. 30 (1950) 57

Table 3—Continued

Number of the compound	Structural formula	Melting point °C	Reference for preparation
4		210	J.Prakt.Chem. [2], 52, 128 (1895)
5		151	Ber.55, 1295 (1922)

Useful image results are obtained in the process of the present invention with said thiol or thione compounds in a weight ratio of at least 1:30 to 1:1 with respect to the spiropyran compound. The N-vinylcarbazole polymer or copolymer is preferably used as binding agent so that it is present in a large molar excess with respect to the spiropyran compound.

The spiropyran compound(s) is (are) preferably used in admixture with a 5- to 20-fold amount by weight of photosensitive organic halogen compound such as carbon tetrabromide.

This ratio, however, is not limitative since useful results are obtained with, e.g., the spiropyran and photosensitive polyhalogen compound in a ratio by weight in the range of 1:1 to 1:50.

In order to diminish the rate of spontaneous thermal colour formation over long periods of time as might be encountered during storage of the recording material and its processing, so-called anti-foggants may be added to the photosensitive composition. Suitable anti-foggants include triaryl compounds of group V elements, e.g. triphenylstibine and sterically hindered phenols, e.g. 2,6-di-tert.butyl-p-cresol and other reducing agents or compounds accepting atmospheric oxygen. Triphenylstibine and analogous compounds for the purpose of the present invention are described in the United Kingdom Pat. No. 1,071,104.

Preferred amounts of anti-foggant agent such as triphenylstibine are within the weight ratio range of 1:100 to 10:100 with respect to photosensitive carbontetrabromide and/or iodoform.

A dry photographic coating containing the above mentioned ingredients may be formed by dissolving the binding agent(s) in a suitable inert solvent that acts as dispersing or dissolving medium for the other ingredients and that is removed from the coating composition by evaporation so that a solid photographic recording layer is left 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 in an oxygen-free environment before the exposure.

For that purpose hydrophobic polymers are used preferably as binding agent. They shield the ingredients from a direct contact with the atmosphere and more especially from oxygen as much as possible.

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

When no self-supporting layer is produced these polymers may be used in admixture for improvement of the mechanical strength or adhering power of the recording layer to its subbed or non-subbed support.

Suitable subbing layers for photochromic layers containing a spiropyran compound are described in the Belgian Pat. No. 782,026. Said subbing layers applied to a polyester film support are made of a partially saponified copolymer of vinyl chloride and vinyl acetate and/or of a polymer or copolymer of acrylic or methacrylic acid esters of aliphatic or cycloaliphatic alcohols containing from 1 to 8 carbon atoms.

It has been established experimentally that the adherence of recording layers containing poly-N-vinylcarbazole or copolymers containing N-vinylcarbazole units to polyester resin supports can be markedly improved by using in admixture with the N-vinylcarbazole polymer or copolymer a polyester, a phenoxy resin or a phenol-formaldehyde resin. A preferably applied polyester resin is polyethylene isophthalate.

A preferred phenoxy resin is EPONOL 55-B-40 of Shell, the Netherlands.

Suited phenol-formaldehyde resins are:  
 the polycondensation product of a mixture of p-cresol and phenol with formaldehyde (50:50),  
 the polycondensation product of a mixture of p-tert.butylphenol and phenol with formaldehyde,  
 the polycondensation product of p-cresol and formaldehyde (used in excess)  
 a xylenol-formaldehyde resin like RESIN R 70 of British Resin Products, Great-Britain.

The resins improving the adherence are preferably used in a percentage by weight calculated on the recording layer of at least 3 percent.

The infrared exposure of the recording materials used according to the present invention may proceed in any known thermographic copying apparatus of the reflectographic type. A suitable operating temperature is in the range of 90° to 150°C.

The recording materials are suited to produce coloured copies of image-wise infrared-absorbing originals, the colour of the dye-image being determined by the type of spiropyran compound used.

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

According to a preferred embodiment the stabilization proceeds with increased speed when the recording layer is first overall heated at about 80°C in the absence of visible light for at least 5 sec, and then treated with a chlorinated solvent, e.g. perchloroethylene at room temperature (20°C) for at least 15 sec in order to extract the photosensitive polyhalogen compound.

Stabilization may proceed very fast by dipping the exposed recording material in a heated organic liquid having a relatively high boiling point, preferably above 200°C and not affecting the recording layer. The organic liquid is preferably heated in the range of 145° to 165°C and the dipping time is e.g. 5 to 20 sec.

Suitable liquids are mineral oil of aliphatic or naphthenic nature e.g. motor oil and ISOPAR G (trade name). A post-treatment with a solvent, e.g. a chlorinated hydrocarbon solvent may be necessary to remove the residual oil film.

The present invention is illustrated by the following examples. The percentages are by weight unless otherwise indicated.

#### EXAMPLE 1

A photosensitive composition consisting of:

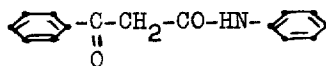
0.12 g of carbon tetrabromide  
0.12 g of iodoform  
0.1 g of 3-methyl-di- $\beta$ -naphtho-spiropyran  
0.03 g of triphenylstibine  
0.06 g of acetanilide and  
8 ml of a 5 percent solution of poly-N-vinylcarbazole in methylene chloride,  
was applied to a non-subbed polyethylene terephthalate support in a thickness of 0.12 mm. The layer was dried at room temperature.

The photosensitive film obtained was exposed reflectographically in a 3M Thermofax copying machine (Model 47) in contact with an opaque original being a black printed text on white paper. A dense blue positive image of the original was obtained.

The copy as such was not stable to light and had to be stabilized by heating at 170°C.

#### EXAMPLE 2

A same photosensitive composition as in example 1 was used, with the difference, however, that 0.06 g of compound having the following formula:



was substituted for 0.06 g of acetanilide. A same thermographic exposure step as in example 1 was executed.

Positive blue images showing no fog were obtained. Fixation of the image against any further action of light had to be executed by heating at 170°C.

#### EXAMPLE 3

A photosensitive composition consisting of:

0.15 g of carbon tetrabromide  
0.15 g of iodoform  
0.04 g of di- $\beta$ -naphthospiropyran  
0.01 g of 2-mercaptobenzothiazole  
0.025 g of triphenylstibine, and  
10 ml of 5 percent solution of poly-N-vinylcarbazole in methylene chloride,

was applied to a non-subbed polyethylene terephthalate support in a thickness of 0.12 mm. Drying was done at 50°C.

The same circumstances of exposure as in example 1 yielded a positive blue copy of the original. A very faintly fogged background was formed. Stabilisation of the image against light was also achieved by a thermal treatment at 170°-180°C.

#### EXAMPLE 4

A photosensitive composition consisting of:

200 ml of 5 percent solution of poly-N-vinylcarbazole in a mixture of methylene chloride and trichloroethane (3:1)  
2.5 g of carbon tetrabromide  
2.5 g of iodoform  
2.5 g of trimethyldi- $\beta$ -naphthospiropyran  
0.8 g of triphenylstibine, and  
0.2 g of 2-mercaptobenzothiazole

was applied to a non-subbed polyethylene terephthalate support by means of a knife coater. The thickness of the wet layer was such that the coverage of the applied composition amounted to 91 g per sq.m.

Reflectographic exposure of the photosensitive film in a 3M Thermofax (Model 47) apparatus in contact with an opaque original yielded very dense positive blue images without background fog.

In order to make the images stable to light an additional thermal treatment was necessary.

#### EXAMPLE 5

Same compositions as mentioned in example 4 were produced with the difference, however, that other spiropyran compounds were used, viz. compounds 4, 9, 15, 22 and 26 of Table 1 yielding blue, magenta, yellow and cyan images respectively.

## 25

## EXAMPLE 6

A photosensitive composition consisting of:

- 0.15 g of carbon tetrabromide
- 0.05 g of iodoform
- 0.1 g of 3-methyl-di- $\beta$ -naphthospiropyran
- 0.01 g of 2-mercaptobenzothiazole, and
- 10 ml of a 5 percent solution of polystyrene in a mixture of methylene chloride and trichloroethylene (1:1)

was applied in a thickness of 0.12 mm to a non-subbed polyethylene terephthalate support. The layer was dried at room temperature.

Reflectographic exposure proceeded according to the arrangement of FIG. 1 in a 3M Thermofax photocopier, model secretary, set at the lowest transport speed and yielded a very dense positive reproduction of the original.

## EXAMPLE 7

A photosensitive composition consisting of:

- 0.12 g of carbon tetrabromide
- 0.12 g of iodoform
- 0.16 g of 3-methyl-di- $\beta$ -naphthospiropyran
- 0.04 g of triphenylstibine
- 0.01 g of 2-mercaptobenzothiazole, and
- 10 ml of a 5 % solution of poly-N-vinylcarbazole in a mixture of methylene chloride and trichloroethane (1:1)

was applied in a thickness of 0.12 mm on tracing paper. The film was dried at 50°C.

Reflectographic exposure in a 3M Thermofax Dry Photocopier model 47 (medium speed), according to the arrangement indicated in FIG. 2 yielded a directly legible positive image.

## EXAMPLE 8

- 0.1 g of carbon tetrabromide
  - 0.1 g of iodoform
  - 0.1 g of 3-methyl-di- $\beta$ -naphthospiropyran
  - 0.025 g of triphenyl stibine, and
  - 0.5 g of poly-N-vinylcarbazole
- were dissolved in a mixture of 5 ml of methylene chloride and 5 ml of trichloroethylene.

This composition was applied in a thickness of 0.12 mm to a non-subbed polyethylene terephthalate support and drying was done at 50°C.

Reflectographic exposure according to the arrangement of FIG. 1 in a 3M Thermofax Photocopier Model 47 with low transport speed yielded a very dense blue positive reproduction of the original.

## EXAMPLE 9

To a photosensitive composition containing:

- 0.12 g of carbon tetrabromide
- 0.12 g of iodoform
- 0.1 g of 3-methyl-di- $\beta$ -naphthospiropyran
- 0.03 g of triphenylstibine
- 0.06 g of acetanilide, and
- 8 ml of a 5 % solution of poly-N-vinylcarbazole in a mixture of methylene chloride and dichloroethane (50:50).

## 26

were added 0.50 g of a 4 % solution of polyethylene isophthalate in methylene chloride. The mixture obtained was coated on a polyethylene terephthalate support in such a way that after drying at 40°C a layer of 0.12 mm was obtained.

The material obtained was exposed and processed as described in Example 1. A deep blue image in a very good adhering scratch-resistant recording layer was obtained.

The same good results were obtained by replacing the polyethylene isophthalate respectively by:

RESIN R 70 (trade name of British Resin Products, Great Britain, for a xlenol-formaldehyde resin)

a copolycondensate of p-cresol and phenol with formaldehyde (50/50)

a polycondensate of p-cresol and formaldehyde

a copolycondensate of p-tert.butyl-phenol and phenol with formaldehyde.

## EXAMPLE 10

A photosensitive composition consisting of:

- 0.12 g of carbon tetrabromide
- 0.12 g of iodoform
- 0.1 g of 3-methyl-di- $\beta$ -naphthospiropyran
- 0.035 g of triphenylstibine
- 0.060 g of acetanilide
- 0.50 g of a 4 % solution of polyethylene isophthalate in methylene chloride, and
- 8 ml of a 5 % solution of poly-N-vinylcarbazole in a mixture of methylene chloride and dichloroethane (50:50)

was coated on a polyethylene terephthalate support in such a way that after drying at 40°C a layer of 0.12 mm was obtained.

The material obtained was exposed as described in Example 1.

The stabilization of the image proceeded according to one embodiment by heating the recording layer whilst pressing it for 10 sec. in contact with a metal roller heated at 85°C. Subsequently, the recording material was dipped for 15 sec at room temperature (20°C) into perchloroethylene. The image thus obtained was stable to daylight and had an optical density of 1.80.

The stabilization could equally well be effected according to a second embodiment by dipping the exposed material for 5 sec. in ISOPAR G (trade name of Shell Company, the Netherlands, for a mixture of hydrocarbons boiling in the range of 166–170°C) heated at 160°C.

The recording layer containing the stabilized image was scratch-resistant and strongly adhered to its support.

The N-vinyl polymers and copolymers containing N-vinylcarbazole units which can be used according to the invention can be prepared by application of one of the various known polymerization procedures, e.g., by pearlor emulsion polymerization or by polymerization in solution. The initiation of the polymerization can occur by free radicals, by ion formation, or by radiation e.g., with actinic light. The polymerization degree is not critical and may vary between wide limits. As far as the copolymers are concerned, the content of groups corresponding to the general formula given hereinbefore is not critical and, as shown hereinafter in the table of copolymers containing N-vinylcarbazole units, it may

vary between wide limits, e.g. between 20 and 95 percent, in accordance with the desired 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 percent.

The preparation of suitable poly-N-vinylcarbazoles is described e.g. in the German Pat. Nos. 931,731, 936,421, 1,097,680 and 1,158,367 and the U.S. Pat. No. 2,072,465.

The preparation of suitable N-vinylcarbazole copolymers is described in the United Kingdom Pat. No. 964,875, 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) ( $R_1 = H$ ,  $R_2 = H$ ,  $A = -CH_2-$ ).

Halogen-substituted poly-N-vinyl carbazoles are described in the published Japanese Patent Applications 21,875/67, 25,230/67, 7,592/68, 19,751/67 and 7,591/68.

For illustrative purposes suitable vinyl copolymers containing N-vinyl carbazole units are enumerated in the following table 4.

Table 4

Copolymer	mole % 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 methyl acrylate	67.6
copolymer of N-vinylcarbazole and ethyl acrylate	41
graft copolymer of N-vinylcarbazole and ethyl-acrylate	90.3
emulsion polymer of N-vinylcarbazole and polyethylacrylate	94.5
copolymer of N-vinylcarbazole and n-butyl acrylate	58.3
copolymer of N-vinylcarbazole and 2-ethyl hexylacrylate	51.6
copolymer of N-vinylcarbazole and acryloxyethyldiethylamine	76.6
copolymer of N-vinylcarbazole and vinylcinnamate	92.5
copolymer of N-vinylcarbazole and methyl methacrylate	62.7
copolymer of N-vinylcarbazole and isobutyl methacrylate	51.8
copolymer of N-vinylcarbazole and lauryl methacrylate	77.4
copolymer of N-vinylcarbazole and methylacryloxethyl 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

Table 4-Continued

Copolymer	mole % of N-vinyl-carbazole
5 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
10 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

We claim:

1. A process for forming a dye image comprising applying a heat pattern having a temperature of at least 90°C of the image in the presence of minor amounts of about up to 20% of visible light to a recording material including a recording layer containing an intimate mixture comprising:

- at least one spiropyran compound of the group consisting of a spirodibenzopyran, a spirodinaphthopyran, a spirobenzonaphthopyran, a 1,3,3-trimethylindolinobenzospiropyran, a 1,3,3-trimethylindoline-naphthospiropyran, or a spiropyran that contains a condensed aromatic nucleus of anthracene or phenanthrene, and
- at least one ultra-violet radiation-sensitive polyhalogen compound capable of producing on exposure with ultra-violet radiation with the spiro-pyran compound a dye salt and having the general formula:



wherein:

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

- one of said groups A, B, X or Y is an alkyl group, an aryl group or an aroyl group and the other groups are each chlorine, bromine, or iodine, or two of said groups A, B, X or Y each is an aromatic acyl group and the other groups chlorine, bromine, or iodine, and in working relation with said mixture at least one of the following compounds,

a. a tautomeric organic nitrogen containing compound corresponding to the following general formula:



in which:

X represents oxygen, sulphur, selenium or the group



in which R is hydrogen, or an alkyl, allyl, or phenyl group, and



Z represent the necessary atoms to close a 5- or 6-membered heterocyclic nitrogen-containing ring system, and

b. a polymer containing N-vinylcarbazole units.

2. A process according to claim 1, wherein the pattern-wise heating of the recording material proceeds by exposure thereof to infrared radiation and a minor amount of visible light while said layer is in heat-conductive contact with an original containing infrared-absorbing image markings.

3. A process according to claim 2, wherein the exposure to said infra-red radiation and visible light is a reflectographic exposure.

4. A process according to claim 3, wherein said layer is applied to a support transparent for infrared radiation and visible light and said exposure is made through said support.

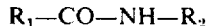
5. A process according to claim 3, wherein said layer is applied to a support that is heat-conductive and said exposure is made through said layer while said support is in contact with said original markings.

6. A process according to claim 1, wherein the polyhalogen compound is carbon tetrabromide.

7. A process according to claim 1, wherein the polymer containing N-vinylcarbazole units is poly-N-vinylcarbazole serving as binding agent for said layer.

8. A process according to claim 1, wherein the layer contains also an amido, acylamino, or ureido compound.

9. A process according to claim 8, wherein said amido, acylamino or ureido compound corresponds to the following general formula:



wherein:

$R_1$  represents an organic residue of the type present in a carboxylic acid chloride, a  $-NHR_3$  or



group in which each of  $R_3$  and  $R_4$  represents an alkyl group,

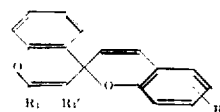
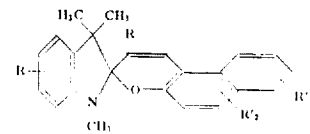
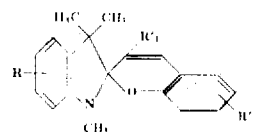
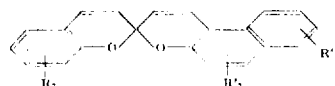
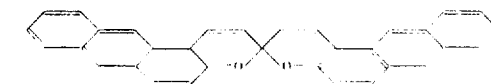
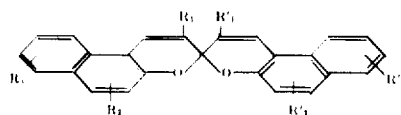
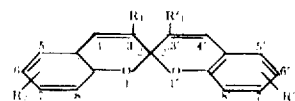
$R_2$  represents hydrogen or an organic residue.

10. A process according to claim 1, wherein the material is preliminarily treated to stabilize the eventual dye image by uniformly heating the recording layer in the absence of visible light at a temperature of about 80°C and then treating it with perchloroethylene at room temperature.

11. A process according to claim 1, wherein the dye image is stabilized by dipping the exposed recording material in an inert organic liquid heated between 145° and 165°C.

12. The process of claim 1 wherein said spiropyran compound corresponds to one of the general formulae:

30



35

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 carbon atoms in the 3 and 3' positions together.

13. The process of claim 1 wherein said layer is pattern-wise heated to a temperature in the range of about 90°-150°C.

14. The process of claim 1 wherein said nitrogen compound is used in a ratio by weight of about 1:30 to about 1:1 relative to said spiropyran compound.

15. The process of claim 1 wherein said spiropyran compound is used in a ratio of about 1:5 to about 1:50 relative to said polyhalogen compound.

\* \* \* \* \*

60

65