United States Patent [19]

Kampfer et al.

[11] **3,816,131**

[45]* **June 11, 1974**

[54] **PHOTOGRAPHIC DRY COPYING PROCESS**

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[73] Assignee: **Agfa-Gevaert Aktiengesellschaft,** Leverkusen, Germany

[*] Notice: The portion of the term of this patent subsequent to Oct. 9, 1990, has been disclaimed.

[22] Filed: **Aug. 23, 1971**

[21] Appl. No.: **174,270**

[30] **Foreign Application Priority Data**

Aug. 25, 1970 Germany 2042054

[52] **U.S. Cl.** ..... **96/29 D,** 96/48 HD, 96/67, 117/36.2

[51] **Int. Cl.** **G03c 5/5,** G03c 1/72

[58] **Field of Search** ..... 96/29 D, 48 HD, 88–90 R, 96/66 T, 119 R

[56] **References Cited**

UNITED STATES PATENTS

3,619,237 11/1971 Leclair 117/36.2

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Assistant Examiner—Alfonso T. Suro Pico
Attorney, Agent, or Firm—Connolly and Hutz

[57] **ABSTRACT**

Certain halogenated methine dyes make improved sensitizers for light-sensitive photographic layers containing the sensitizer and an image-producing compound capable of transfer at 80°–200°C. to an image-receiving layer in contact with the photographic layer, but rendered non-transferrable where exposed to light.

26 Claims, No Drawings

PHOTOGRAPHIC DRY COPYING PROCESS

The invention relates to a photographic dry copying process and to a light-sensitive material for carrying out this process.

Dry photographic processes for producing copies of an original are already known per se. The materials used for these processes are usually materials which contain layers that are sensitive to light or heat. These layers are exposed imagewise to light or heat, which initiates a color-producing reaction and which leads to formation of the image.

The known light-sensitive materials of the type mentioned above which can be used for producing negative copies have, however, numerous disadvantages. Their sensitivity to light is unsatisfactory, especially in the visible region of the spectrum, so that the copying times required are too long and reproduction of colored originals is difficult.

Moreover, the finished copies are still sensitive to light, and stabilization of these copies to daylight can generally only be achieved by a complicated after-treatment.

Processes for the production of copies by imagewise exposure of a light-sensitive layer which contains a light-sensitive compound and an image-producing compound which can be transferred to an image-receiving layer are also known. In such processes, the image-producing compound is converted in the exposed areas into a non-transferable compound. When the exposed layer is brought into contact with an image-receiving layer which contains compounds which react with the image-producing compound to form colored compounds, and the layers are heated while in contact with each other to a sufficiently high temperature, the image-producing compound from the unexposed areas of the light-sensitive layer is transferred to the image-receiving layer.

One such process, for example, is the so-called heat development process in which light-sensitive materials having a silver halide emulsion layer which contains a photographic developer substance, are used. After exposure, development is carried out by heating the light-sensitive material in contact with an image-receiving layer which contains substances, that react with the developer substance to produce dyes. The developer substance in the unexposed areas of the light-sensitive layer is transferred by the heat into the image-receiving layer so that a colored image is produced in these areas of the receiving layer.

One disadvantage of these known heat development

or developer sublimation processes is that the silver halide emulsion layers which contain developer are insufficiently stable in storage. This instability is due to the fact that these layers contain substances which increase the residual moisture of the layers, e.g. salts which form hydrates, or glycols, and is also due to the increased sensitivity to oxidation of most developer substances in these unhardened or only slightly hardened emulsion layers which have a high residual moisture content.

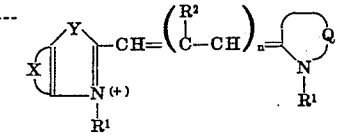
A process which belongs to this type of copying process is described in U.S. Pat. No. 3,094,417 and uses light-sensitive layers which contain a transferable compound and a dye. On exposure, the transferable compound (4-methoxy-1-naphthol) is converted into a non-transferable product. This compound is transferred by subsequent heating from the unexposed areas into an image receiving layer where it reacts with a silver salt (silver behenate) to produce a colored positive image.

The last mentioned process has the disadvantage that the sensitivity of the layers is relatively low and, moreover, the keeping quality of the material is limited.

It is among the objects of the present invention to provide photographic dry copying processes and light-sensitive materials suitable for these processes, which materials should have sufficient sensitivity to light, be sufficiently stable, contain dyes which render the material sensitive to the spectral region required, and which enable multicolored or black- and-white images to be produced.

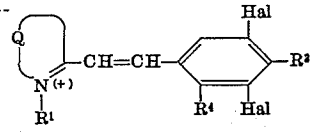
We now have found a process for the production of copies by imagewise exposure of a light-sensitive layer which contains a sensitiser and an image-producing compound transferrable to an image-receiving layer, the image-producing compound in the exposed areas being converted into a non-transferable compound and the exposed layer being brought into contact with an image-receiving layer which contains compounds which react with the image-producing compounds to form colored compounds and the layers which are in contact with each other being heated to a temperature at which the image-producing compound in the unexposed areas of the light-sensitive layer is transferred to the image-receiving layer, wherein the light-sensitive layer contains, as sensitizers, halogenated methine dyes of the formulae shown below, and, as image-producing, transferable compound, a reducing agent which is transferable at a temperature of between 80°C and 200°C and which is converted into non-volatile reduction products upon exposure.

I.



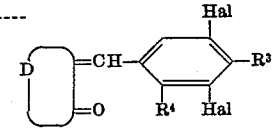
Anion (−).

II.



Anion (−).

III.



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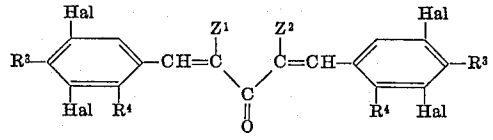

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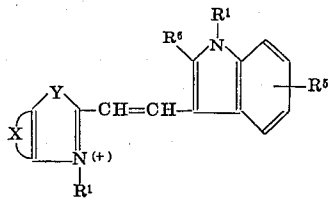


Anion(−).

wherein

Hal = Cl, Br or I;

R^1 = 1) a saturated or unsaturated aliphatic group having preferably up to six carbon atoms which may be substituted, e.g. with halogen such as chlorine or bromine or with phenyl, hydroxyl, amino, carboxyl, sulfo, sulfamino, sulfamoyl, carboxylamino, carbamoyl, alkoxycarbonyl, alkoxy, aroxy, carboxyalkyl, sulfato or thiosulfato groups;

2) cycloalkyl such as cyclohexyl, or

3) aryl, in particular a group of the phenyl series;

R^2 = hydrogen, alkyl having preferably up to three carbon atoms, aryl such as phenyl, or cycloalkyl such as cyclohexyl;

R^3 and R^4 may be the same or different and represent hydrogen or hydroxyl but at least one is a hydroxyl group;

R^5 = hydrogen, alkyl or alkoxy having preferably up to five carbon atoms, halogen, in particular chlorine,, bromine or iodine, trifluoromethyl or aryl, especially a phenyl group;

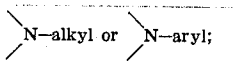
R^6 = aryl such as phenyl, heterocyclic rings such as thienyl, or furyl, which may also be substituted;

X = the ring members required to complete a benzene or naphthalene ring which contains at least one halogen such as Cl, Br or I, or trifluoromethyl;

Z^1 and Z^2 = hydrogen, alkyl having preferably up to three carbon atoms or alkoxycarbonyl groups having preferably up to four carbon atoms;

Z^1 and Z^2 may also together represent the methylene groups required to complete a 5-membered or 6-membered ring;

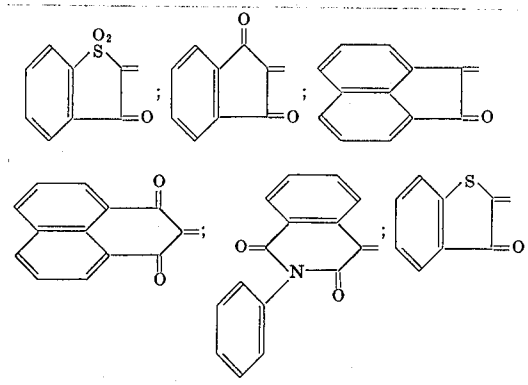
Y = O, S, Se, —CH=CH—,



Anion = any anion, e.g. halide such as chloride, bromide or iodide, perchlorate, sulfate, methyl sulfate, p-toluene sulfate and the like; the anion is absent in cases where R^1 contains an acid group in the anionic form so that a betaine is present;

n = 0, 1 or 2;

D = the ring members required to complete an isocyclic or heterocyclic ketomethylene ring; these rings may be the usual ketomethylene rings of cyanine chemistry, for example those of the rhodanine series such as 3-ethyl rhodanine, 3-allyl rhodanine or 3-cyclohexyl rhodanine, those of the 2-thio-2,4-oxazolidinedione series such as 3-ethyl-2-thio-2,4-oxazolidinedione, those of the thiohydantoin series such as 1,3-dimethyl-2-thiohydantoin or 1-methyl-3-phenyl-2-thiohydantoin, those of the barbituric acid or thiobarbituric acid series such as 1,3-diethyl-thiobarbituric acid or 1,3-diphenylthiobarbituric acid, those of the isoxazolone, oxindole, 2-thio-2,5-thiazolidinedione or 2,4-imidazolidinedione series, or the ketomethylene rings characterised by the following structural formulae:

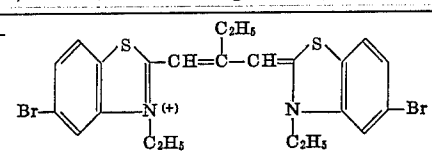


Q = the members required to complete a 5-membered or 6-membered heterocyclic ring, which heterocyclic ring may contain a condensed benzene or naphthalene ring and other substituents; the heterocyclic rings may be the usual heterocyclic rings of cyanine chemistry, for example those of the thiazole series (e.g. thiazole, 4-methylthiazole, 5-methylthiazole, 4,5-dimethylthiazole, 4-phenylthiazole, 5-phenylthiazole, 4,5-diphenylthiazole, benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 6-bromobenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5,6-dimethylbenzothiazole, 4-phenylbenzothiazole, 5phenylbenzothiazole, 6-phenylbenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-ethoxybenzothiazole, 6-ethoxybenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-(methylenedioxy)benzothiazole, 5-diethylaminobenzothiazole, 6-diethylaminobenzothiazole, 5-carboxybenzothiazole, 5-sulphobenzothiazole, tetrahydrobenzothiazole, 7-oxotetrahydrobenzothiazole, naphtho (1,2-d)thiazole, naphtho (2,1-d)-thiazole, 5-methoxynaphtho (2,1-d)thiazole, 5-ethoxynaphtho (2,1-d)thiazole, 7-methoxynaphtho (2,1-d)-thiazole, 8-methoxy-naptho (1,2-d)thiazole, etc.), those of the selenazole series (e.g.

4-methylselenazole or 4-phenylselenazole benzoselenazole, 5-chlorobenzoselenazole, 5,6-dimethylbenzoselenazole, 5-hydroxybenzoselenazole, 5-methoxybenzoselenazole, tetrahydrobenzoselenazole, naphtho (1,2-d)selenazole or naphtho (2,1-d)selenazole), those of the oxazole series (e.g. oxazole, 4-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, benzoxazole, 5-chlorobenzoxazole, 6-chlorobenzoxazole, 5,6-dimethylbenzoxazole, 5-phenylbenzoxazole, 5-hydroxybenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 6-dialkylaminobenzoxazole, 5-carboxybenzoxazole, 5-sulphobenzoxazole, 5-sulphonamido-benzoxazole, 5-β-carboxyvinyl-benzoxazole, naphtho-(1,2-d)oxazole, naphtho (2,1-d)oxazole or naphtho-(2,3-d)oxazole), those of the imidazole series (e.g. 1-methylimidazole, 1-ethyl-4-phenylimidazole, 1-butyl-4,5-dimethylimidazole, etc. 1-methylbenzimidazole, 1-butyl-4-methylbenzimidazole, 1-ethyl-5,6-dichlorobenzimidazole, 1-ethyl-5-trifluoromethyl-benzimidazole, 1-methylnaphtho-(1,2-d)imidazole or 1-ethylnaphtho-(2,3-d)imidazole), those of the 3,3-dialkylindolenine series (e.g. 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,-3-dimethyl-5-methoxyindolenine, etc.), those of the pyridine series (e.g. pyridine, 3-methylpyridine, 4-methylpyridine, 6-methylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 3,6-dimethylpyridine, 4,6-dimethylpyridine, 4-chloropyridine, 5-chloropyridine, 6-chloropyridine, 3-hydroxypyridine, 4-hydroxypyridine, 4-phenylpyridine, 6-phenylpyridine, etc.), those of the 4-pyridine series (e.g. 2-methylpyridine, 3-methylpyridine, 2,3-dimethylpyridine, 2,6-dimethylpyridine, 2-hydroxypyridine, quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, 5-oxo-5,6,7,8-tetrahydroquinoline, isoquinoline or 3,4-dihydroisoquinoline), those of the thiazoline series (e.g. thiazoline, 4-methylthiazoline, etc.), and those of the pyrroline, tetrahydropyridine, thiadiazole, oxadiazole, pyrimidine, triazine or benzothiazine series. The heterocyclic rings and aryl groups may be further substituted in any manner, e.g. with additional alkyl groups which preferably have up to three carbon atoms, such as methyl or ethyl, or with halogen such as chlorine, bromine or iodine, the trifluoromethyl group, hydroxyl, alkoxy preferably with up to three carbon atoms such as methoxy or ethoxy, hydroxyalkyl, alkylthio, aryl such as phenyl or aralkyl such as benzyl, amino, substituted amino and the like.

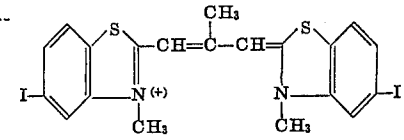
The following are examples of suitable compounds: (Tos. standing for tosyl)

1.



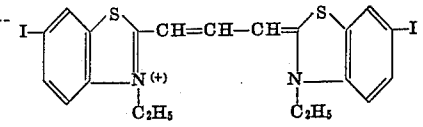
Br(-)

2.



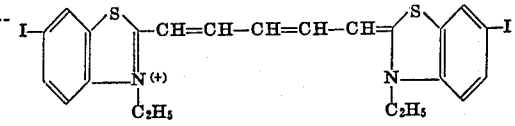
$CH_3SO_4^{(-)}$

3.



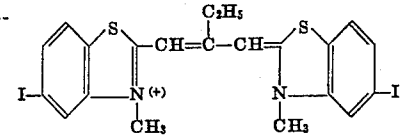
Br(-)

4.



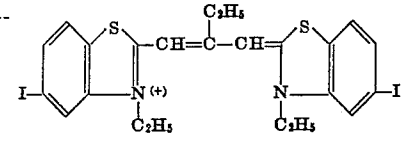
Tos.(-)

5.



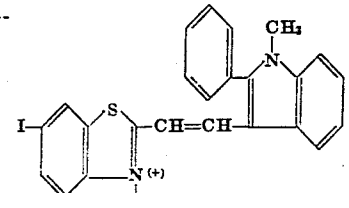
Br(-)

6.



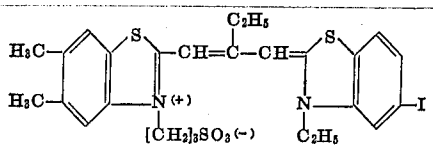
$CH_3SO_4^{(-)}$

7.



$ClO_4^{(-)}$

8.....



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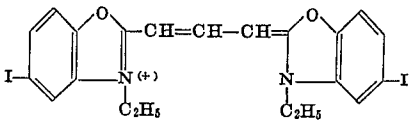
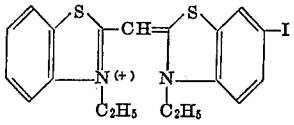


Br(-)

10.....



Tos.(-)

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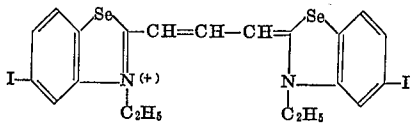

Tos.(-)

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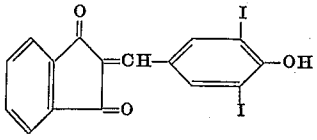

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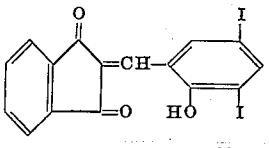

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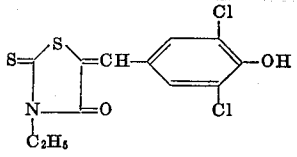

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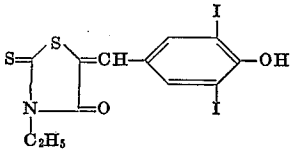

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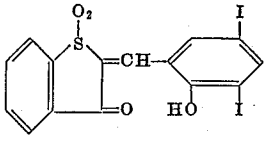

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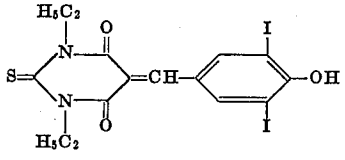

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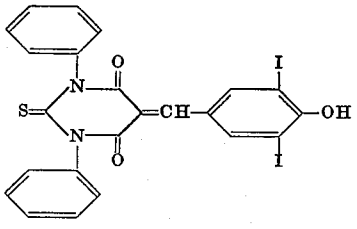

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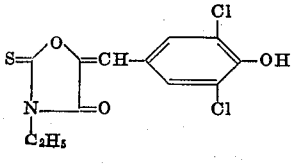

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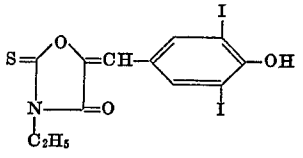

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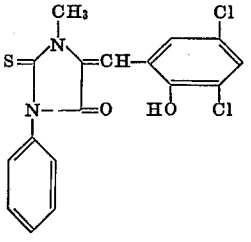

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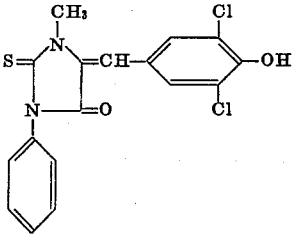

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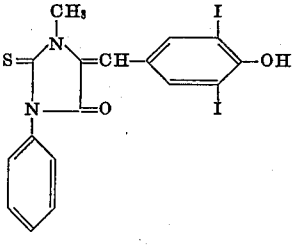

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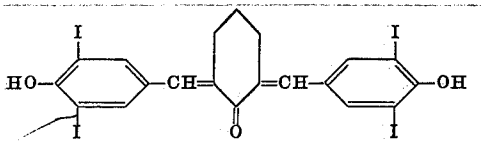
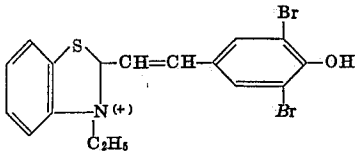
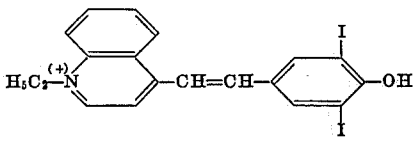


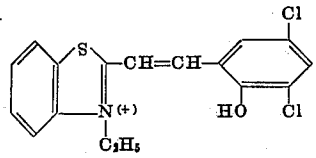
25..... Tos. (−).



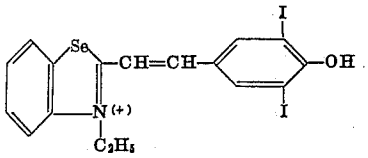
26..... Tos. (−)



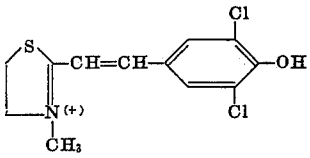
27..... Cl(−)



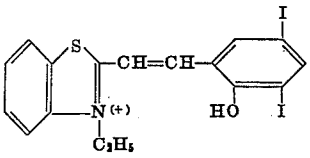
28..... Tos. (−)



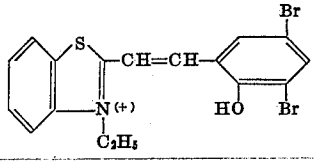
29..... Cl(−)



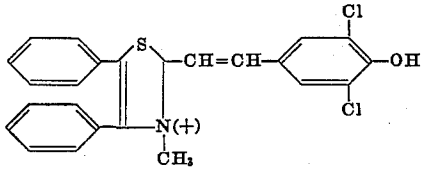
30..... Tos. (−)



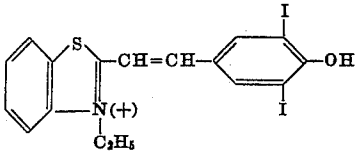
31..... Tos. (−)



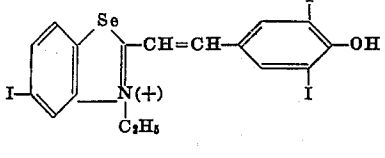
32..... Cl(−)



33..... Tos. (−)



34..... Tos. (−)



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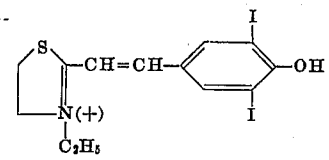
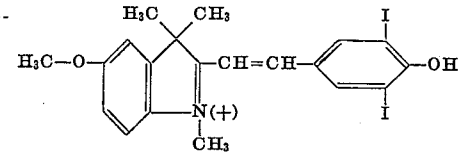


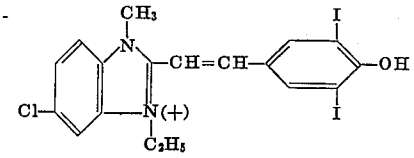
$C_2H_5—SO_4^{(-)}$

36.....



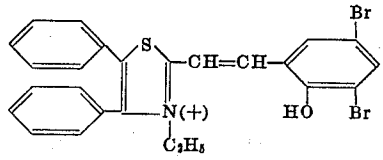
$I^{(-)}$

37.....



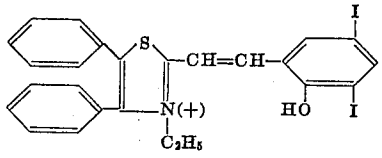
$C_2H_5—SO_4^{(-)}$

38.....



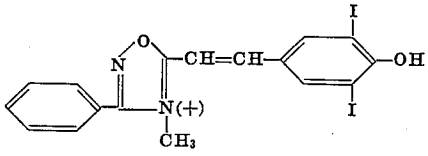
$C_2H_5—SO_4^{(-)}$

39.....



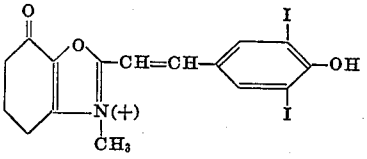
$C_2H_5—SO_4^{(-)}$

40.....



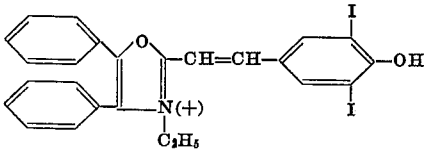
$J^{(-)}$

41.....



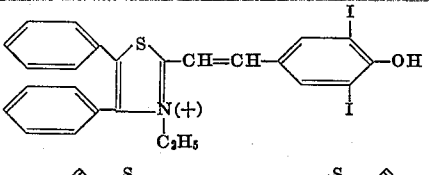
$J^{(-)}$

42.....



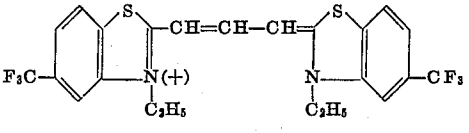
$C_2H_5—SO_4^{(-)}$

43.....



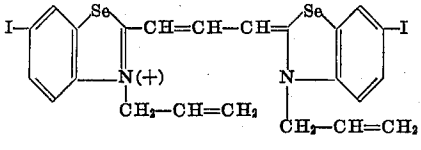
$C_2H_5—SO_4^{(-)}$

44.....



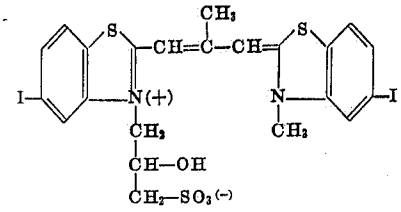
$C_2H_5—SO_4^{(-)}$

45.....

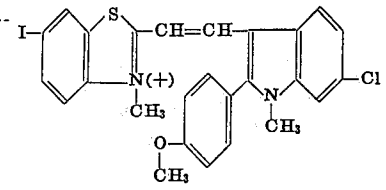


$Br^{(-)}$

46.....

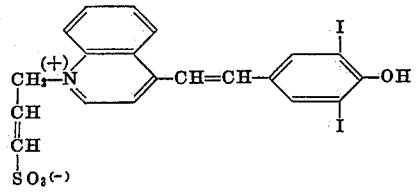


47.....

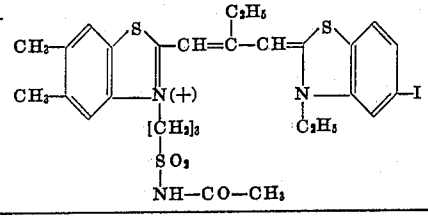


$ClO_4^{(-)}$

48.....



49.....



$ClO_4^{(-)}$

The mono-, tri- and penta-methine cyanines of formula I may be synthesized by known methods (see e.g. F.M. Hamer "The Cyanine Dyes and Related Compounds," 1964). The dyes of formulae II to V are obtained by condensing 2-methyl quaternary salts of heterocyclic bases or ketomethylene compounds with the appropriate aldehydes in solvents such as alcohol, pyridine or glacial acetic acid to which is added a base such as triethylamine or piperidine.

The preparation of compounds 17 and 28 is described in detail below. The other compounds are obtained in analogous manner.

Compound 17

2.0 g of 1,3-diethyl-thiobarbituric acid and 3.7 g of 3,5-diiodo-4-hydroxybenzaldehyde in 30 ml of glacial acetic acid are refluxed for 5 minutes with the addition of 3 ml of piperidine. The mixture is cooled and the dye is removed by suction filtration and recrystallised from methanol. 3.6 g of the dye are obtained. m.p. = 248°C (decomposition).

Compound 28

4.0 g of 2-methyl-3-ethyl-benzoselenazole-tolylsulfonate and 3.7 g of 3,5-diiodo-4-hydroxybenzaldehyde in 50 ml of alcohol with the addition of 2 ml of triethylamine are heated on a steam bath for 15 minutes. The dye precipitates after a short time. The mixture is cooled and the dye is removed by suction filtration, washed with alcohol and recrystallised from dimethyl formamide. 3.7 g, m.p. = 237°C (decomposition).

The image-producing compounds must meet the following conditions:

1. They must react with the sensitizers defined above upon exposure to form non-transferable reaction products. 2. They must be transferable at temperatures of between 80° and 200°C to the image-receiving layer.
3. They must be capable of reacting with the compounds of the image-receiving layer to form colored reaction products at the temperature of between 80° and 200°C.

The following reducing agents, for example are particularly suitable image-producing compounds:

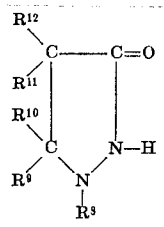
1. Phenols and naphthols, especially compounds of the benzene and naphthalene series containing at least two aromatic hydroxyl groups which may be partly etherified such as 1-hydroxy-4-alkoxy-naphthalenes, or which are substituted with hydroxyl and an amino group or a substituted amino group which in the case of benzene derivatives are situated in the para- or ortho-position, e.g. the compounds shown in Table 1 below.

TABLE 1

1-hydroxy-4-methoxynaphthalene,
1-hydroxy-4-ethoxynaphthalene,
1-hydroxy-2-methyl-4-methoxynaphthalene,
4,4'-dimethoxynaphthalene-1,1'-dihydroxy-2,2'-binaphthyl,
1,4-dihydroxynaphthalene,
1-hydroxy-4-aminonaphthalene,
1,2,3-trihydroxy-5-acetylbenzene,
methyl-3,4,5-trihydroxybenzoate,
ethyl-3,4,5-trihydroxybenzoate,
1,2,3,4-tetrahydro-8-hydroxyquinoline,
1-[2'-methylsulfonamidoethyl]-1,2,3,4-tetrahydro-6-hydroxyquinoline,
4-methylaminophenol,
4-isopropylidene-aminophenol,
4-aminophenol,
4-hydroxyanilino-methane sulfonic acid,
4-hydroxy-3-methylanilino-methane phosphonic acid,
1-hydroxy-4-propoxynaphthalene.

Also suitable as image-producing compounds are the aminophenol developers described in German Patent Specification Nos. 1,159,758; 1,200,679; 1,203,129 and 1,203,605.

2. Pyrazolidone-(3) derivatives of the following formula:



wherein

R^8—represents hydrogen, alkyl or aryl which may be substituted, for example with lower alkyl or alkoxy or with halogen, and

R^9,R^{10},R^{11} and R^{12} represent hydrogen, alkyl, aryl or a substituted alkyl or aryl group.

The compounds shown in the following table have been found to be suitable.

TABLE 2

1-phenyl-3-pyrazolidone,
1-m-tolyl-3-pyrazolidone,
1-p-tolyl-3-pyrazolidone,
1-phenyl-4-methyl-3-pyrazolidone,
1-phenyl-5-methyl-3-pyrazolidone,
1,4-dimethyl-3-pyrazolidone,
4-methyl-3-pyrazolidone,
4,4-dimethyl-3-pyrazolidone,
1-phenyl-4,4-dimethyl-3-pyrazolidone,
1-(m-chlorophenyl)-4-methyl-3-pyrazolidone,
1-(p-chlorophenyl)-4-methyl-3-pyrazolidone,
1-(m-chlorophenyl)-3-pyrazolidone,
1-(p-chlorophenyl)-3-pyrazolidone,
1-(p-tolyl)-4-methyl-3-pyrazolidone,
1-(o-tolyl)-4-methyl-3-pyrazolidone,
1-(p-tolyl)-3-pyrazolidone,
1-(m-tolyl)-3-pyrazolidone,
1-(m-tolyl)-4,4-dimethyl-3-pyrazolidone,
1-(2'-trifluoroethyl)-4,4-dimethyl-3-pyrazolidone,
5-methyl-3-pyrazolidone

The above compounds may be prepared by the methods described in British Patent Specification Nos. 679,677 and 679,678, the "phenimines" which can be obtained by reacting acrylonitrile derivatives with the corresponding hydrazine compounds being saponified to 3-pyrazolidones.

3-Pyrazolidones may also be prepared by the process described in British Patent Specification No. 703,669, the end products being obtained by the direct condensation of esters of acrylic acid or derivatives thereof with hydrazines. This process is particularly suitable for reaction with hydrazine itself. The 3-pyrazolidones thus obtained, which have an oily consistency, can be obtained in the form of crystalline compounds by converting them into salts, e.g. hydrochlorides, sulfates or naphthalene-1,5-disulfonates. The preparation of the 4,4-dialkyl-3-pyrazolidones has been described in U.S. Pat. No. 2,772,282. In this process, 2,2-dialkyl-β-chloropropionic acid chlorides are reacted with hydrazines.

3-Pyrazolidones may be used as free bases or in the form of their salts.

3. N,N-dialkylphenylene diamine derivatives, especially those in which the alkyl groups contain preferably up to three carbon atoms and the phenylene nucleus may be substituted by alkyl or alkoxy groups.

The free primary amino group may be blocked, for example in the form of a Schiff's base by reacting it with aldehydes, especially benzaldehyde, or it may be blocked by a sulfomethyl group which may be introduced by a Mannich reaction. The phenylene diamine derivatives which have a blocked primary amino group are particularly suitable because stable layers can easily be produced by means of these compounds.

The compounds shown in the following table have been found to be suitable.

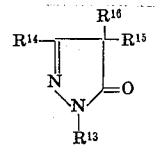
TABLE 3

N,N-diethyl-p-phenylene diamino sulfate,
N,N'-dibenzylidene-p-phenylene diamine,
N,N-diethyl-N'-sulfomethyl-p-phenylene diamine,
N,N-dimethyl-N'-sulfomethyl-p-phenylenediamine,
3-methyl-4-sulfomethylamino-N,N-diethylaniline,
N-benzylidene-N',N'-diethyl-p-phenylene diamine,
3-methoxy-4-sulfomethylamino-N,N-diethylaniline.

The image-producing substances of the type shown above are known per se. Methods of preparing them can be found in German Patent Specification Nos. 1,159,758 and 1,203,129, and in the literature.

4. Pyrazolin-5-one derivatives: It is preferred to use those pyrazolin-5-one derivatives which contain at least one hydrogen in the 4-position or a 4-aminophenylamino group.

Pyrazolin-5-one compounds of the following formula are preferred:



wherein

R^{13} = (1) hydrogen,

(2) a saturated or olefinically unsaturated aliphatic group having preferably up to 6 carbon atoms, which group may be substituted, e.g. with phenyl as in the benzyl group, with cyano, with halogen, e.g. fluorine, with an amino group which may itself be substituted, e.g. alkylated amino groups, especially dialkylamino, the alkyl groups of the alkyl amino group preferably containing up to three carbon atoms,

(3) aryl, especially a group of the phenyl series, and the aryl ring may itself be substituted, e.g. with alkyl or alkoxy which preferably contains up to three carbon atoms, nitro, halogen such as fluorine, chlorine or bromine, amino, substituted amino groups, e.g. alkylated amino groups,

(4) a heterocyclic group, e.g. benzothiazolyl, or

(5) cycloalkyl such as cyclohexyl or cyclopentyl;

R^{14} = (1) hydrogen,

(2) a saturated or olefinically unsaturated aliphatic group having preferably up to six carbon atoms, which aliphatic group may be substituted, e.g. with phenyl as in the case of a benzyl or phenylethyl, with halogen such as fluorine, chlorine or bromine, with alkoxycarbonyl, with hydroxyl or alkoxy,

(3) aryl, especially a group of and the phenyl series, the aryl ring may be substituted, e.g. with alkyl

or alkoxy which preferably has up to three carbon atoms, with nitro or with halogen such as chlorine or bromine,

(4) a heterocyclic group, e.g. pyridyl,

(5) cycloalkyl such as cyclohexyl or cyclopentyl,

(6) hydroxyl which may be etherified, especially with short chain aliphatic radicals having up to three carbon atoms,

(7) an amino group which may be substituted e.g. with alkyl which preferably has up to three carbon atoms, .

(8) alkoxycarbonyl having up to five carbon atoms;

R^{15} 32 (1) hydrogen,

(2) a saturated or olefinically unsaturated aliphatic group having preferably up to six carbon atoms, which may be substituted, e.g. with phenyl as in the case of benzyl or phenylethyl groups, with halogen such as chlorine or bromine, with cyano or with alkoxy, alkoxycarbonyl or anilinocarbonyl,

(3) aryl, especially a group of the phenyl and series, the aryl ring may be substituted, e.g. with alkyl or alkoxy which preferably has up to three carbon atoms, nitro or cyano,

(4) an amino group which may be substituted, e.g. with alkyl which has preferably up to three carbon atoms, cycloalkyl, phenyl or acyl and especially acyl groups of short chain aliphatic carboxylic acids,

(5) alkoxy having preferably up to three carbon atoms;

R^{16} = hydrogen or a 4-aminophenylamino group or 4-dialkylaminophenylamino group.

In addition, R^{14} and R^{15} taken together may stand for the members required for completing a 5- or 6-membered carbocyclic or heterocyclic ring.

Suitable compounds are shown in the following table where for the first 33 listings R^{16} is hydrogen.

TABLE 4

Pyrazolin-5-one No.	R^{13}	R^{14}	R^{15}
1	C_6H_5	NH_2	H
2	H	CH_3	H
3	C_6H_5	CH_3	H
4	cyclohexyl	CH_3	H
5	p-tolyl	CH_3	H
6	m-chlorophenyl	CH_3	H
7	2,5-dichlorophenyl	CH_3	H
8	3-nitrophenyl	CH_3	H
9	4-nitrophenyl	CH_3	H
10	C_6H_5		
$COOC_2H_5$	H		
11	1-phenylethyl	C_6H_5	H
12	C_6H_5		
$CH_2COOC_2H_5$	H		
13	C_6H_5	pyridyl-4	H
14	2-diethylaminoethyl	CH_3	H
15	2,4,6-trichlorophenyl	CH_3	H
16	2,4,5-trichlorophenyl	CH_3	H
17	2-cyanoethyl	C_6H_5	H
18	3,5-dimethylphenyl		
$COOC_2H_5$	H		
19	C_6H_5	OH	H
20	3-nitrophenyl	CH_3	CH_3
21	3-aminophenyl	CH_3	CH_3
22	3-nitrophenyl	CH_3	benzyl
23	2-ethoxyphenyl	C_6H_5	CH_3
24	C_6H_5	C_6H_5	CH_3
25	C_6H_5	C_6H_5	C_2H_5
26	C_6H_5	$-CH_2-CH_2-CH_2-CH_2-$	
27	C_6H_5	CH_3	$-CH_2-CO-NHC_6H_5$
28	C_6H_5		
$COOC_2H_5$	CH_3		
29	C_6H_5	$-CH_2-CH_2-CH_2-S-$	
30	3-nitrophenyl	CH_3	C_2H_5
31	C_6H_5	CH_3	
$NHCOCH_3$			
32	C_6H_5		
$COOC_2H_5$			
OC_2H_5			
33	C_6H_5	CH_3	CH_3
34	1-[benzothiazolyl-2']-3,4-dimethyl-4-[4-diethylaminophenylamino]-pyrazolin-5-one		
	1-phenyl-3,4-dimethyl-4-[4-diethylamino-phenylamino]-pyrazolin-5-one		

The pyrazolin-5-one derivatives are prepared by methods known from the literature, e.g. the monograph by R.H. and Wiley "Pyrazolones, Pyrazolidones and Derivatives" (1964) and German Patent Specification No. 1,155,675.

The light-sensitive layers contain at least one sensitizer in quantities of 10 to 300 mg/m^2 and one or more image-producing compounds in quantities of 0.02 to 0.5 g/m^2. This range of concentrations has been found to be suitable although concentrations outside this range may, of course, be employed. The concentration depends mainly on the requirements of the given reproduction process.

Particularly suitable combinations of sensitizers with image-producing reducing agents can be found by simple tests. Suitable test methods for this purpose will be described hereinafter. The choice of solvent and of the binding agent used for producing the light-sensitive layer is also important for obtaining optimum results. Particularly suitable combinations of the components used for any particular purpose can be determined by the usual tests well known to the ordinary skilled person.

To produce the light-sensitive layer, sensitizer and image-producing compound may be suspended or dissolved in solvents and mixed with the binding agent and applied to the layer support.

The usual natural or synthetic film-forming polymers are suitable as binding agents for the light-sensitive layer, e.g. proteins, especially gelatin, cellulose derivatives, especially cellulose ethers, cellulose esters or carboxymethyl cellulose, alginic acid and its derivatives, starch ether or gallactomannane, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate, polyvinyl acetate or completely or partly saponified polyvinyl acetate or copolymers of vinyl acetate, for example with olefines such as ethylene or propylene and copolymers of momomers of acrylic- or methacrylic acid or derivatives thereof such as esters, amides or nitriles, etc.. The light-sensitive layers may be used as self-supporting layers or applied to a support. Suitable supports are e.g. paper, especially baryta-coated or polyolefine-coated, more particular polyethylenecoated paper and cellulose esters, e.g. cellulose triacetate, polyesters, especially those based on ethylene terephthalate, glass, etc.

The image receiving material advantageously consists of an image receiving layer applied to a suitable support. Substantially the same substances as those described above for the light-sensitive material are suitable as binding agent for the image receiving layer or as the layer support.

When choosing a binder for the light-sensitive layer and the image receiving layer, care should be taken to ensure that the layers will not stick at elevated temperature. These difficulties, however, are well known from other transfer processes, e.g. the silver salt diffusion process or heat development processes, and can easily be solved by making use of the experience gained in these known fields.

The image receiving layer contains compounds which should be insensitive, or as restricted as possible in their sensitivity, to visible light under the conditions of the process of the invention, and which react with the transferred image producing compounds to form colored products. Numerous compounds have been found suitable for this purpose. Chemically, these compounds belong to a wide variety of classes so that their systematic chemical classification is not possible. However, suitable compounds or suitable combinations of an image producing compound arranged in the light-sensitive layer and of the reactant for the image-forming reaction in the image receiving layer can be sufficiently clearly defined by simple laboratory tests customarily employed in the art. Thus, for example, the two reactants must react when briefly heated for a few seconds to a temperature of between about 80° and 200°C to form a stable dye. A second test must then be carried out to choose suitable image producing compounds. The purpose of this test is to show whether the image producing compound will react sufficiently rapidly with the light-sensitive azide on exposure to light, so that, when the mixture is heated after it has been exposed, it will not produce a colored compound with the reactant in the image receiving layer.

The following classes of compounds are examples of suitable compounds in the image receiving layer for reaction with the image transferred from the light-sensitive layer.

1. Heavy metal compounds, especially compounds of metals of Groups III a V *a* and to Groups I *b*, II *b*, VI *b*, VII *b* and VIII of The Periodic Table e.g. compounds of the following heavy metals:

cadmium, mercury, iron, cobalt, nickel, copper, silver, gold, bismuth or thallium. Salts of these metals with long chained aliphatic, carboxylic acids are especially suitable, e.g. nickel stearate, cobalt palmitate, iron stearate, and the addition compound of bismuth nitrate with amines such as triethanolamine. It is found to be especially suitable to use silver compounds which are substantially insensitive to light under the conditions of the copying process according to the invention, e.g. the silver salts described in U.S. Pat. No. 3,330,663, i.e. silver salts of aliphatic carboxylic acids having a thioether group or silver salts of long-chained fatty acids such as silver behenate, silver palmitate or silver stearate, etc, containing eight to 24 carbon atoms. When the above-mentioned heavy metal compounds are used, brown to black copies are obtained. The image consists of the particular metal and/or a reaction product of the transferred image producing compound.

2. The image-receiving layer may also contain oxidising agents and dye components which react imagewise with the transferred image-producing compound to yield dyes by oxidative coupling, e.g. the known color couplers of color photography which couple with oxidised phenylenediamine derivatives to yield dyes, or compounds which in their oxidised form react under oxidising conditions with e.g. pyrazolin-5-one compounds to yield colored coupling products. Suitable reactants are e.g. the oxidation products of p-phenylene diamines or their derivatives which react with pyrazolin-5-one compounds to yield azomethine dyes of the type known in conventional color photography.
3. Diazonium salts which react with the transferred reducing agents, e.g. the aminophenols, aminonaphthols, phenylene diamine derivatives or pyrazolin-5-one compounds to form a colored product. This reaction is similar in principle to that used in the known photographic diazo-type process.
4. Leucophthalocyanines are also suitable for use as reactants for the reaction which produces the image dye. Leucophthalocyanines which have not or could not be prepared from finished phthalocyanines are known as phthalocyanine precursors. This term is used, for example, in the article by B. R. A. Brooks, J. G. Burt, B. F. Skiles and M. S. Whelen, J. Org. Chem. 24, page 383 (1959). In the relevant chapter in Ullmanns Encyklopadie der Technischen Chemie, 3rd Edition, Volume 13, the term "phthalocyano-metal complexes" is used for the same type of materials for which in the present context the term "leucophthalocyanines" is used. The last mentioned expression is explained e.g. in U.S. Pat. No. 2,772,285. Although that patent refers only to leuco copper phthalocyanine, its explanation is also applicable analogously to the corresponding complexes with other metals which form phthalocyanines. Leucophthalocyanines according to this definition are colorless or only slightly colored products in which the phthalocyanine structure is already completely formed, and which can be converted into phthalocyanines by a reduction process. In this reduction process, constituents which the leucophthalocyanine molecule contains in addition to phthalocyanine may also be split off. Such leucophthalocyanines may be prepared e.g. by first preparing a phthalocyanine, e.g. a phthalocyanine which is free from metal or CuPc (Pc =

phthalocyanine), NiPc, CoPc or ZnPc and then treating the phthalocyanine with additional ligands under oxidising conditions, or by heating a reaction mixture which is in itself suitable for the preparation of a phthalocyanine to a temperature slightly below that required for the preparation of the phthalocyanine, or by carrying out the reaction without the reduction potential required for formation of the phthalocyanine.

Leucophthalocyanines which contain metal are more suitable for this reaction because those which are free from metal are relatively unstable. The highly stable and only slightly colored leuco cobalt phthalocyanines are especially suitable. Especially to be mentioned are the leuco cobalt phthalocyanines which are described in Angewandte Chemie, 68, page 145 (1956), e.g. the phthalocyanine cobalt ethylene diamine complex. Instead of ethylene diamine, other diamines or polyamine may also be used as ligands, for example propylene diamine-(1,2), and -(1,3), monoethylpropylene diamine-(1,3), hydroxyethylethylene diamine, N-methyl-N-β-hydroxyethylpropylene diamine, N,N'-diethylethylene diamine, N,N-di-(β-aminoethyl)-ethylene diamine, N,N'-di-(β-aminoethyl)-ethylene diamine or N,N-di-[β-(β-aminoethyl)-aminoethyl]-amine or also monoamines such as 3-(2'-ethylhexyloxy)-propylamine-(1) or stearylamine. The solubility properties of the leuco-CoPc depend on the type of amine used in the molecule.

In another embodiment of the process of the present invention, color-forming reactants can be eliminated altogether from the image-receiving layer. This applies e.g. in the case where there are used image-producing compounds, for example phenols or naphthols, which yield sufficiently colored compounds when heated alone or in the presence of atmospheric oxygen. In that case, the image-receiving material used may be plain, uncoated paper.

In addition to the image-producing reactants, the image-receiving layers may contain other additives which advantageously influence the color tone, contrast, stability, etc. of the copy. Image-receiving layers of this type are already known and have been described, for example, in German Auslegeschrift Nos. 895,101; 1,003,577; 1,159,758; 1,004,043 and 1,165,410, in Dutch Patent Specification No. 277,086, in U.S. Pat. No. 3,335,006 and in Belgian Patent Nos. 614,064 and 609,057.

The image-receiving layers may also contain white pigments, e.g. zinc oxide, silicon dioxide or titanium dioxide as fillers, for improving the whites and for controlling the tendency of the layers to stick, and they may contain terpene resins and organic acids for improving the stability in storage. Image-receiving layers of this type have been described in U.S. Pat. Nos. 3,074,809 and 3,107,174.

The color tone of the images produced can be influenced e.g. with compounds of the 1-(2H)-phthalazinone series; toners of this type have been described in U.S. Pat. Nos. 3,080,254 and 3,446,648. Additives which accelerate the reduction process in the image-receiving layer have also been found to be advantageous. Sterically hindered phenols such as 2,6-di-tert-butyl-p-cresol, for example, are suitable for this purpose. Compounds of this type have been described in U.S. Pat. No. 3,218,166. The image tone and image density may also be improved by certain metal salts, e.g. copper-II stearate. Metal ion image intensifiers of this kind and their application have been described in German Auslegeschrift No. 1,572,209.

The usual light sources may be used for exposing the light-sensitive layers according to the invention such as mercury lamps, quartz iodine lamps or incandescent lamps. The spectral sensitivity of the light-sensitive material depends on the nature of the dye or of the combination of dye and reducing image producing compound.

Exposure may be either contact exposure, optical exposure or reflection exposure.

Transfer of the image-producing compounds from the unexposed areas of the light-sensitive layers to the image-receiving layer is performed by heating at temperatures of between 80° and 200°C. Heating may be effected e.g. by passing the exposed light-sensitive layer in contact with the image-receiving layer over hot plates or rollers or by exposure to infra-red light. The most suitable temperature and heating time depend, of course, on the nature of the image-producing compound and can easily be determined by a few simple tests.

The material according to the invention may also be modified in that the image-receiving layer and light-sensitive layer may be combined on one support. In that case, it is necessary to use a transparent layer support on which the image-receiving layer, e.g. a layer containing silver behenate dispersed in a copolymer of styrene or isobutylene, is applied first, and the light-sensitive layer, e.g. an ethyl cellulose layer which contains the sensitiser and the reducing agent, is then applied on the image-receiving layer.

The sensitivity of these light-sensitive layers can be advantageously increased or extended to other regions of the spectrum in a manner depending on the absorption of the compounds according to the invention by combining the dyes which are to be used according to the invention with dyes which can be reduced by a process of photoreduction, e.g. the dyes mentioned in U.S. Pat. No. 3,094,417, e.g. erythrosine.

EXAMPLE 1

Light-sensitive Material

The following casting solution is applied to a layer support of pergamyn:

30	mg of Dye No. 30,
50	mg of 1-hydroxy-4-methoxy naphthalene,
2.5	g of ethyl cellulose as a 5% solution in butanone-2 and
150	ml of butanone-2.

The layer is dried in the usual manner.

The image-receiving material is prepared by grinding the following components in a ball mill for 6 hours:

2.1	g of a mixture of 1 mol silver behenate, and 1 mol behenic acid,
1.66	g of terpene resin,
0.86	g of 1-(2H)-phthalinone,
4.8	g of zinc oxide,
0.56	g of silica gel,
0.37	g of 2,6-di-tertiary-butyl-4-methyl phenol,
0.034	g of tetrachlorophthalic acid anhydride,
15	g of an 8 percent solution of ethyl methacrylate in pentanone-3,
80	g of a 1.5 percent solution of polyvinyl acetate in butyl acetate, and
30	g of butyl acetate,

and applying the resulting mixture to paper and drying it.

When dry, the layer contains about 0.2 g of silver per m^2 in the form of silver behenate.

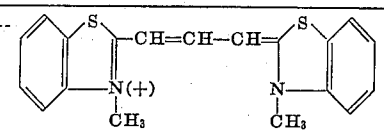
Processing

The light-sensitive material is exposed behind a wedge to a 1000 Watt iodine quartz lamp from a distance of 30 cm for 5 minutes.

The exposed layer is then brought into contact with the image-receiving layer and heated to a temperature of 125°C for 10 seconds or heated in an ordinary commercial heat development apparatus. The results were compared using each of the above-listed dyes as well as the following non-halogenated dyes, and are shown in Table 5:

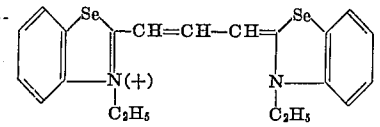
Comparison Dye

A.....



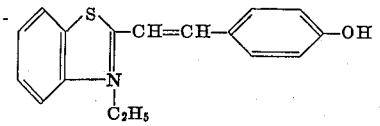
Tos.(-)

B.....



I(-)

C.....



Cl(-)

D.....

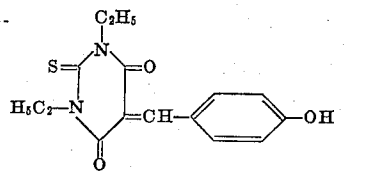


Table 5

Dye No.	Steps $\sqrt{2}$	Dye No.	Steps $\sqrt{2}$
Comparison dye A	—	20	2–3
Comparison dye B	—	21	4
Comparison dye C	—	22	3
Comparison dye D	—	23	4
1	1–2	24	1–2
2	6	25	4
3	3	26	4
4	3	27	4
5	7	28	5
6	11	29	1
7	5–6	30	11
8	1–2	31	7
9	2	32	6
10	1	33	5
11	6	34	6
12	2	35	5
13	6	36	9
14	1	37	2–3
15	2	38	10
16	2	39	12
17	5	40	9
18	7	41	3
19	2	42	12
		43	12

EXAMPLE 2

Light-sensitive Material

The following casting solution is applied to a layer support of parchment paper.

30	mg of Dye No. 17
50	mg of 1-hydroxy-4-methoxy naphthalene,
2.5	g of ethyl cellulose, and
150	ml of ethyl acetate.

The layer is dried in the usual manner.

Processing

The light-sensitive material is exposed through a positive transparent original to an ordinary 1000 Watt incandescent lamp (tungsten filament) at a distance of 5 to 10 cm for 30 seconds.

Instead of a transparent original, a text printed on ordinary paper may be used as original. The exposure to reflected light which is necessary in this case should be carried out for a period of between 15 and 25 seconds under otherwise the same conditions.

The exposed layer is then brought into contact with the image-receiving layer described in Example 1 and the two layers are heated to a temperature of 125° to 140°C for 5 to 20 seconds or treated in an ordinary commercial heat development apparatus.

A sharp, positive black copy of the original is obtained.

Instead of Dye 17 and instead of the image-producing compound mentioned above, other combinations may be employed. The results are summarised in Table 6 below.

TABLE 6

Dye No.	Image-producing compound	Quantity in mg	Colour of the copy
17	1-hydroxy-5-methoxy naphthalene	50	grey black
5	compound 7 of Table 4		grey black
30	do. 33 do.	150	grey black
5	do. 26 do.	150	grey black
30	do. 20 do.	100	grey black
30	1,2,3,4-tetrahydro-8-hydroxy quinoline	50	black brown
30	1-phenyl-3-pyrazolidone	50	dark brown
5	1-phenyl-5-methyl-3-pyrazolidone	50	dark brown
30	N-benzylidene-N',N'-diethyl-p-phenylene diamine	50	dark brown
30	1-phenyl-5-methyl-3-pyrazolidone	50	dark brown

Instead of silver behenate used in the image-receiving layer in this case, other silver compounds may be used, e.g. silver stearate or silver salts of octadecylmercaptoacetic acid, 2-octadecylmercapto-5-carboxymethylmercapto-1,3,4-thiadiazole (as described in U.S. Pat. No. 3,330,663), etc. The choice of suitable compounds depends on the purpose for which they are to be used and the required color of the image.

EXAMPLE 3

Light-sensitive Material

A light-sensitive layer is prepared from a solution of:

30	mg of Dye 5,
100	mg of N,N-diethyl-N'-sulfomethyl-p-phenylene diamine,
100	mg of sodium acetate,
100	ml of ethanol, and
50	ml of a 1.5 percent solution of a cellulose ether in ethanol

by casting the solution on paper and drying it.

Image-receiving material

A layer is prepared from a solution of:

1.5	g of 1-phenyl-3-methyl-pyrazolone-(5),
1	g of sodium bromate,
35	ml of water, and
15	ml of a 5% aqueous polyvinyl alcohol solution,

by casting the solution on paper and drying it.

Processing

Processing is carried out as in Example 2. A red positive is obtained.

EXAMPLE 4

Light-sensitive Material

A light-sensitive layer is prepared as in Example 3 from:

30 mg of Dye 5,
100 mg of N,N-diethyl-N'-sulfomethyl-p-phenylene diamine,
100 mg of sodium acetate,
100 ml of ethanol, and
50 ml of a 1.5 percent solution of a cellulose ether in ethanol.

Image-receiving Material

A layer is prepared on a paper support from:

150 mg of N,N-diethyl-p-aminophenyl-diazonium chloride zinc chloride complex,
10 ml of water, and
5 ml of a 1.5 percent aqueous solution of a cellulose ether.

Processing

Processing is carried out as in Example 2. A brown positive is obtained.

EXAMPLE 5

Light-sensitive Material

A light-sensitive layer is prepared from a solution of:

30 mg of Dye 5,
100 mg of 1-(2,5-dichlorophenyl)-3-methyl-pyrazolin-5-one,
2.5 g of ethyl cellulose, and
150 ml of ethyl acetate.

The solution is applied to a layer support of pergamyn in the usual manner and dried.

Image-receiving Layer

The following casting solution is applied to a layer support of baryta paper:

5 g of 4-dimethylamino-benzene-diazonium tetrafluoroborate,
1 g of saponin,
1 g of polyoxyethylene hydroxyethyl cellulose, and
100 ml of water.

Processing

Processing is carried out as described in Example 2. A positive red image of the original is obtained on a grey background.

EXAMPLE 6

Light-sensitive material as in Example 1.

Image-receiving Material

50 mg of a leuco cobalt phthalocyanine stearylamine complex prepared by the method described below are dissolved in 40 g of a 1.5 percent solution of polyvinyl acetate in acetone and 26 g of a 4 percent solution of cellulose acetate in acetone, cast on paper and dried.

Processing

Processing is carried out as described in Example 2. A blue positive of the original is obtained.

The leuco-CoPc used was prepared as follows:

50 g of a crude product prepared according to Example 1 of German Patent Specification No. 855,710 were converted into the nitrate by treatment with concentrated nitric acid as described in German Patent Specification No. 839,939. 16 g of the dried nitrate were boiled in 50 ml of cleaning petrol with 15 g of stearylamine for 20 minutes, the mixture was diluted with 750 ml of cleaning petrol, the resulting solution was filtered at 100°C and stirred cold for several hours and the product which crystallised was removed by suction filtration and dried. The filtered off product, which was obtained in a yield of 27 g, was dissolved in boiling ethanol, the solution was stirred cold, and the crystalline product which then formed was removed by suction filtration and dried. 12 g of an orange coloured substance are obtained.

50 mg of 1-phenyl-5-methyl-3-pyrazolidone may be used as image-producing compound with the same result instead of using 1-hydroxy-4-methoxy naphthalene.

EXAMPLE 7

Light-sensitive material as in Example 1.

Image-receiving Material

An image-receiving material is prepared from:

5 g of iron(III) chloride,
2 g of nitrilotriacetic acid, and
30 ml of a 5 percent aqueous solution of polyvinyl alcohol.

The solution is neutralised with ammonia and cast on paper.

Processing is carried out as described in Example 2. A cyan positive is obtained.

EXAMPLE 8

Light-sensitive material as in Example 1.

Image-receiving Material

1 g of bismuth nitrate is shaken in a ball mill with
40 g of a 1.5 percent solution of polyvinyl acetate in acetone, and
26 g of a 4 percent solution of acetyl cellulose in acetone for 6 hours.

The mixture is cast on paper and dried.

Processing

Processing is carried out as described in Example 2. A brown positive is obtained. Instead of bismuth nitrate, 0.6 g of thallium(I) chloride or 0.8 g of mercury(II) bromide may equally well be used in the image-receiving layer.

EXAMPLE 9

Light-sensitive material as in Example 1.

Processing is carried out as described in Example 2, but the image-receiving material is in this case ordinary writing paper. A positive cyan image of the original is obtained.

EXAMPLE 10

Light-sensitive material as in Example 1.

Image-receiving Material

Ammonia is added to a solution of 5 g of copper(II) chloride in 75 ml of H_2O until the precipitate which first forms redissolves, and 30 ml of 5 percent aqueous polyvinyl alcohol are then added. The solution is then cast on paper and dried.

Processing is carried out as described in Example 2. A grey-green positive image of the original is obtained.

EXAMPLE 11

When used in combination with other dyes, e.g. erythrosine which has its sensitivity at 540 nm, the dyes listed in the following table extend the range of sensitivity of the light-sensitive material to the blue or red region of the spectrum.

Light-sensitive Material

The following casting solution is applied to a layer support of polyester and dried:

30 mg of erythrosine,
30 mg of a dye, the number of which is shown in Table 7,
50 mg of 1-hydroxy-4-methoxy naphthalene,
2.5 g of ethyl cellulose, and
150 ml of butanone.

Processing

A set of interference filters is used to determine the

spectral sensitivity of the light-sensitive material. The filters are permeable to the following wavelengths:

350 nm,	390 nm,	405 nm,	435 nm,	480 nm,
505 nm,	515 nm,	540 nm,	550 nm,	570 nm,
590 nm,	605 nm.			

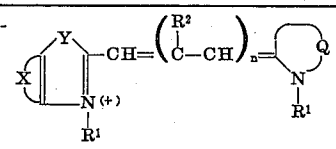
The light-sensitive material is exposed behind the interference filters to a 1000 Watt iodine quartz lamp from a distance of 30 cm for a length of time varying from 5 to 30 minutes according to the individual dye. The exposed material is then brought into contact with the image-receiving layer described in Example 1 and processed in an ordinary commercial heat development apparatus.

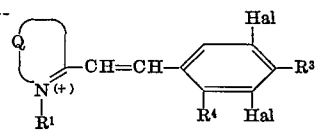
TABLE 7

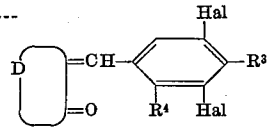
Dye No.	Sensitivity at the following wavelengths
Erythrosine —	540 nm
erythrosine + 9	480, 505, 515, 540 nm
erythrosine + 11	540, 570, 590, 605 nm
erythrosine + 17	480, 505, 515, 540 nm
erythrosine + 26	350, 540, 590, 605 nm
erythrosine + 28	540, 590, 605 nm
erythrosine + 30	540, 590, 605 nm
erythrosine + 33	540, 590, 605 nm
erythrosine + 44	515, 540 nm

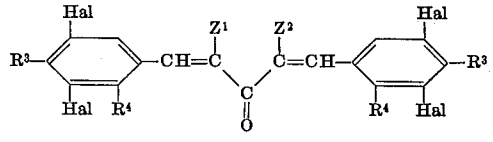
We claim:

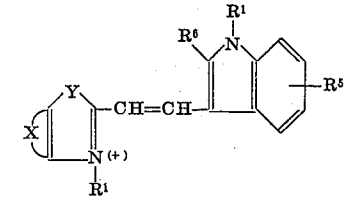
1. In the process for the production of an image by (a) imagewise exposure of a light-sensitive layer which contains a sensitizer and an image-producing compound transferable to an image-receiving layer at temperatures between 80° to 200°C the image-producing compound in the exposed areas being converted in the presence of the sensitizer into a non-transferable compound, and (b) transferring the unconverted image-producing compound to an image-receiving layer and causing it to react in the image-receiving layer to form a colored product, the improvement according to which the sensitizer is at least one halogenated methine dye of the following formulae:

I.  Anion(−).

II.  Anion(−).

III. 

IV. 

V.  Anion(−).

wherein

Hal = Cl, Br or I;

R^1 = (1) a saturated or unsaturated aliphatic group,

(2) cycloalkyl, or

(3) aryl;

R^2 = hydrogen, alkyl, aryl or cycloalkyl;

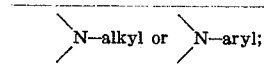
R^3 and R^4 = hydrogen or hydroxyl, but at least one is hydroxyl;

R^5 = hydrogen, alkyl, alkoxy, halogen or aryl;

R^6 = aryl or a heterocyclic ring;

X = the members required to complete a benzene or naphthalene ring which contains at least one halogen or a trifluoromethyl group;

Z^1 and Z^2 separately = hydrogen, alkyl or alkoxycarbonyl, or together stand for the methylene groups required for completing a 5-membered or 6-membered ring;

Y = O, S, Se, —CH=CH—, 

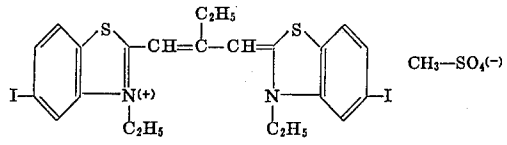
n = 0, 1 or 2;

D = the members required to complete an isocyclic or heterocyclic ketomethylane ring;

Q = the members required to complete a 5-membered or 6-membered heterocyclic ring.

2. The process of claim 1 wherein the sensitizer is a polymethine dye which contains a ring of the phenyl or naphthyl series substituted with at least one iodine atom.

3. The process of claim 2 wherein the sensitizer has the formula:



4. The process of claim 1 wherein the sensitizer has the formula II, and Hal is iodine.

5. The process of claim 4 wherein the sensitizer has a thiazole ring.

6. The process of claim 1 wherein the image-producing compound is a 1-hydroxy-4-alkoxy-naphthalene.

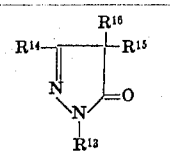
7. The process of claim 6 wherein the image-producing compound is 1-hydroxy-4-methoxy-naphthalene.

8. The process of claim 1 wherein the image-producing compound is 1,2,3,4-tetrahydro-8-hydroxy-quinoline.

9. The process of claim 1 wherein the image-producing compound is a 3-pyrazolidone derivative.

10. The process of claim 9 wherein the image-producing compound is 1-phenyl-4-methyl-3-pyrazolidone.

11. The process of claim 1 wherein the image-producing compound is a pyrazolin-5-one of the formula:



wherein

R^{13} = (1) hydrogen,
(2) a saturated or olefinically unsaturated aliphatic group,
(3) aryl,
(4) a heterocyclic group, or
(5) cycloalkyl;

R^{14} = (1) hydrogen,
(2) a saturated or olefinically unsaturated aliphatic group,
(3) aryl,
(4) a heterocyclic group,
(5) cycloalkyl,
(6) hydroxyl,
(7) amino or
(8) an alkoxycarbonyl group;

R^{15} = (1) hydrogen,
(2) a saturated or olefinically unsaturated aliphatic group,
(3) aryl,
(4) amino, or
(5) alkoxy;

R^{16} = hydrogen or a 4-aminophenylamino group; and

R^{14} and R^{15} together may also represent the members required for completing a carbocyclic or heterocyclic ring.

12. The process of claim 1 wherein the image-receiving layer contains a heavy metal compound which is not sensitive to light under the conditions of the process.

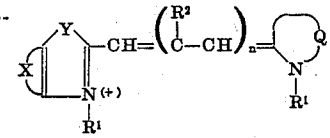
13. The process of claim 12 wherein the image-receiving layer contains a silver compound which has little or no sensitivity to light under the conditions of the process.

14. The process of claim 13 wherein the image-receiving layer contains the silver salt of a long chain aliphatic carboxylic acid having eight to 24 carbon atoms.

15. The process of claim 13 wherein the image-receiving layer contains a silver salt of a thioether-substituted aliphatic carboxylic acid.

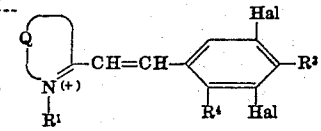
16. In a light-sensitive photographic layer containing a sensitizer and an image-producing compound which can be transferred to an image-receiving layer at temperatures of between 80° and 200°C but which is converted by exposure into a nontransferable reaction product in the presence of the sensitizer, the improvement wherein the sensitizer has the formulae:

I.....



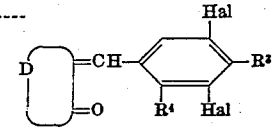
Anion (−).

II.....

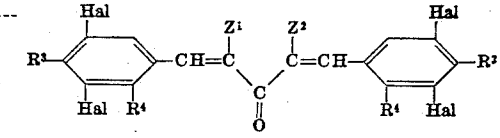


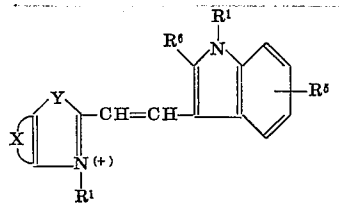
Anion (−).

III.....



IV.....



V----------  Anion(-).

wherein

Hal = Cl, Br or I;

R^1 = (1) a saturated or unsaturated aliphatic group,

(2) cycloalkyl, or

(3) aryl;

R^2 = hydrogen, alkyl, aryl or cycloalkyl;

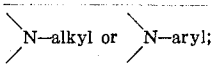
R^3 and R^4 = hydrogen or hydroxyl, but at least one is hydroxyl;

R^5 = hydrogen, alkyl, alkoxy, halogen or aryl;

R^6 = aryl or a heterocyclic ring;

X = the members required to complete a benzene or naphthalene ring which contains at least one halogen or a trifluoromethyl group;

Z^1 and Z^2 separately = hydrogen, alkyl or alkoxycarbonyl, or together stand for the methylene groups required for completing a 5-membered or 6-membered ring;

Y = O, S, Se, —CH=CH—, 

N—alkyl or N—aryl;

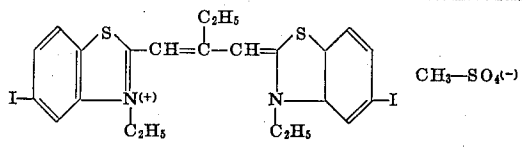
n = 0, 1 or 2;

D = the members required to complete an isocyclic or heterocyclic ketomethylene ring;

Q = the members required for completing a 5-membered or 6-membered heterocyclic ring.

17. The process of claim **16** characterised in that the sensitizer is a polymethine dye which contains at least one iodine atom.

18. The process of claim **17** wherein the polymethine dye has the following formula:



19. The process of claim **16** wherein the image-producing compound is a 1-hydroxy-4-alkoxy-naphthalene.

20. The process of claim **19** wherein the sensitizer has a thiazole ring.

21. The process of claim **16** wherein the image-producing compound is a 1-hydroxy-4-alkoxy-naphthalene.

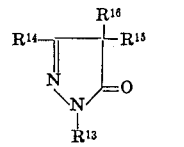
22. The process of claim **21** wherein the image-producing compound is 1-hydroxy-4-methoxy-naphthalene.

23. The process of claim **16** wherein the image-producing compound is 1,2,3,4-tetrahydro-8-hydroxy-quinoline.

24. The process of claim **16** wherein the image-producing compound is a 3-pyrazolidone.

25. The process of claim **24** wherein the image-producing compound is 1-phenyl-4-methyl-3-pyrazolidone.

26. The process of claim **16** wherein the image-producing compound is a pyrazolin-5-one of the formula:



wherein

R^{13} = (1) hydrogen,

(2) a saturated or olefinically unsaturated aliphatic group,

(3) aryl,

(4) a heterocyclic group, or

(5) cycloalkyl;

R^{14} = (1) hydrogen,

(2) a saturated or olefinically unsaturated aliphatic group,

(3) aryl,

(4) a heterocyclic group,

(5) cycloalkyl,

(6) hydroxyl,

(7) amino, or

(8) an alkoxycarbonyl group;

R^{15} = (1) hydrogen,

(2) a saturated or olefinically unsaturated aliphatic group,

(3) aryl,

(4) amino, or

(5) alkoxy;

R^{16} = hydrogen or a 4-aminophenylamino group; and

R^{14} and R^{15} together may also denote the members required to complete a carbocyclic or heterocyclic ring.

* * * * *