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(54) Image forming method and heat-processible color photosensitive material for use in said method.

(57) A method which comprises the steps of: providing a heat-processible color photosensitive material that has at least a light-sensitive silver halide, a reducing agent, a binder and a dye-providing material on a support, which dye-providing material contains either a dye portion represented by the following general formula (1) or a dye portion represented by the following general formula (2) or both; performing imagewise exposure on said photosensitive material; subsequent to or simultaneously with the imagewise exposure, thermally developing said photosensitive material in close contact with an image-receiving material; transferring onto said image-receiving material all or part of the diffusible dye containing said dye portion which is formed from said dye-providing material as a function of development; during or after the transfer, chelating part or all of the diffusible dye with a metal to thereby form an image of the chelated dye in said image-receiving material:

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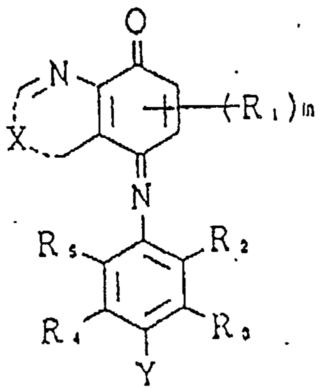
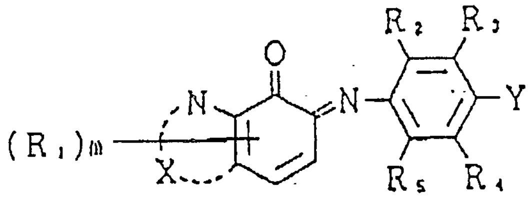
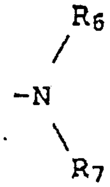


(1)



(2)

where X represent the atomic group necessary to form an aromatic nitrogenous heterocyclic ring; R_1 is a hydrogen atom, a halogen atom or a monovalent organic group; m is an integer of 0 or 1 - 3, provided that when m is 2 or 3, R_1 may be the same or different; Y is a hydroxyl group or a group



$$-N\begin{matrix}R_6\\ R_7\end{matrix}$$

(where R and R_7 each represents a hydrogen atom or an optionally substituted alkyl group); and R^2, R^3, R^4 and R^5 each represents a hydrogen atom, a halogen atom, or a monovalent organic group.

IMAGE FORMING METHOD AND HEAT-PROCESSIBLE COLOR PHOTOSENSITIVE MATERIAL FOR USE IN SAID METHOD

BACKGROUND OF THE INVENTION

The invention relates to a method of forming image by thermal development. More particularly, this invention relates to a method of forming an infrared dye image that can be read with infrared radiation, as well as a heat-processible or thermally developable photosensitive material suitable for use in that method.

One of the efforts presently made in the field of information recording materials such as identification (ID) cards is to make a recording material that contains not only color image information but also character information or signal information such as bar codes. In order to insure rapider information identification or to prevent misidentification, recording materials that carry character information or signal information are often read optically with light longer than 750 nm (which light is hereinafter referred to as "infrared radiation") that is emitted from semiconductor lasers, light-emitting diodes and other light sources.

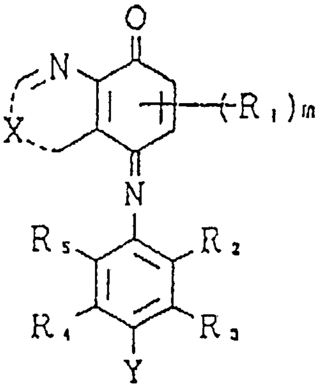
However, even the cyan dye that has an absorption maximum in the longest wavelength range of all the color image forming dyes that are obtained from known heat-processible color phototsensitive materials is almost incapable of absorbing light longer than 750 nm, so it has been practically impossible to record information that can be read with infrared radiation if the heat-processible color photosensitive material of interest is of a type that forms clear color images using the known dyes.

With a view to solving this problem, the present inventors have studied as a heat-processible color photosensitive material that contains a dye-providing material that either forms or releases an infrared dye. However, the heat-processible color photosensitive material still has a need for improvements in various aspects such as the wavelength at which the infrared dye formed absorbs light, its diffusibility and stability under exposure to heat and light. The present invention has been accomplished in order to meet this need.

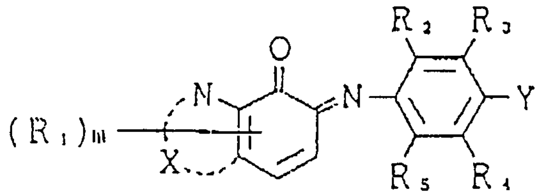
SUMMARY OF THE INVENTION

The principal object of the present invention is to provide a method of forming an infrared dye image that has improved stability under exposed to heat and light and that has a wavelength of absorption that enables reading with infrared radiation at even longer wavelengths, as well as a heat-processible color phototsensitive material that is suitable for use in said method.

As a result of intensive studies conducted in order to attain this object, the present inventors found that it could be attained by a method which comprises the steps of: providing a heat-processible color phototsensitive material that has at least a light-sensitive silver halide, a reducing agent, a binder and a dye-providing material on a support, which dye-providing material contains either a dye portion represented by the following general formula (1) or a dye portion represented by the following general formula (2) or both; performing imagewise exposure on said phototsensitive material; subsequent to or simultaneously with the imagewise exposure, thermally developing said photosensitive material in close contact with an image-receiving material; transferring onto said image-receiving material all or part of the diffusible dye containing said dye portion which is formed from said dye-providing material as a function of development; during or after the transfer, chelating part or all of the diffusible dye with a metal to thereby form an image of the chelated dye in said image-receiving material:

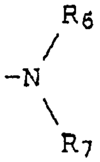


(1)



(2)

where X represents tha atomic group necessary to form an aromatic nitrogenous heterocyclic ring; R_1 is a hydrogen atom, a halogen atom or a monovalent organic group; m is an integer of 0 or 1 - 3, provided that when m is 2 or 3, R_1 may be the same or different; Y is a hydroxyl group or a group



(where R and R_7 each represents a hydrogen atom or an optionally substituted alkyl group); and R^2, R^3, R^4 and R^5 each represents a hydrogen atom, a halogen atom, or a monovalent organic group.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail.

The dye portion represented by the general formula (1) or (2) is usually a cyan dye but when it forms a chelate complex with a transition metal ion, the range of its absorption wavelength shifts to the longer side by at least 100 nm and it becomes an infrared dye. Thus, a heat-processible color photosensitive material that contains a dye-providing material having the dye portion represented by the general formula (1) or (2) (which material is hereinafter referred to as the "compound of the present invention") is capable of forming an infrared dye image and/or a cyan dye image.

The dye portion represented by the general formula (1) or (2) may be pre-chelated (i.e. preliminarily form a chelate with a metal ion) but from the viewpoint of dye diffusibility, it may more preferably be post-chelated, i.e. from a chelate in the image-receiving layer or in a nearby area such as a portion of the image-receiving material other than the image-receiving layer or the topmost layer of the photosensitive material.

The symbol X in each of the general formulas (1) and (2) represents the atomic group necesary to form an aromatic nitrogenous heterocyclic ring, preferably an atomic group capable of forming a condensed pyridine ring.

In each of the general formulas (1) and (2), R_1 represents a hydrogen atom, a halogen atom or a monovalent organic group. A preferred halogen atom is a chlorine or fluorine atom. A preferred monovalent organic group is an optionally substituted alkyl group (e.g. methyl or ethyl), an optionally substituted alkoxy group (e.g. methoxy or ethoxy), $-CONR_6R_7$, $-NHCOR_8$, $-NHCO_2R_8$, $-NHSO_2R_8$, $-NHSO_2NR_6R_7$, $COOR_8$, $-SO_2R_8$, $-NHCOR_6R_7$ or a cyano group, wherein R^6 and R^7 each represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group, and R^8 represents a hydrogen atom, an alkyl group, an aryl group, a cycloalkyl group, a heterocyclic group or an amino group. Each of the groups R_1 and R_6 to R_8 may have a substituent.

When optionally substituted groups such as alkyl, cycloalkyl, aryl and heterocyclic groups are represented by R_1, R_6, R_7 and R_8, illustrative substituents that can be used include a halogen atom (e.g. F or Cl), an alkyl group, an aryl group, a heterocyclic group, a nitro group, a cyano group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a keto group, a sulfonamido group, a sulfamoyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfinyl group, a hydroxyl group, a carboxyl group, and an amino group which may be primary or secondary.

When R_1 represents a halogen atom or a monovalent organic group, at least one R_1 is preferably located in the position ortho to the group $>C = 0$ in the general formula (1) or para to the group $>C = 0$ in the general formula (2).

A hydrogen atom, a halogen atom or a monovalent organic group is represented by each of R_2, R_3, R_4 and R_5 and a preferred halogen atom is chlorine or fluorine. The monovalent organic group may be exemplified by those which are listed in the definition of R_1.

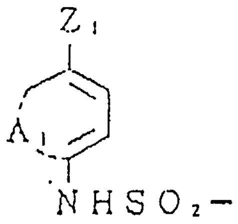
Preferred examples of the alkyl group represented by each of R_6 and R_7 are those which have 1 - 4 carbon atoms such as methyl, ethyl, n-propyl and n-butyl. If these alkyl groups are substituted, preferred substituents include an alkoxy group (e.g. methoxy or ethoxy), an alkylsulfoamide group (e.g. methanesulfoamido), a sulfo group, a carboxy group, a sulfamoyl group, a carbamoyl group, etc.

The dye portion represented by the general formula (1) or (2) preferably forms a metal chelate dye either in the image-receiving layer or in an nearby area. The compound (metal source) that is capable of supplying metal ions to form a metal chelate may be organic or inorganic salts of metal ions (e.g. carboxylates or sulfonates) or it may be one of the complexes (e.g. the metal complexes described in "Chelate Chemistry (5)", ed. by Kagehira Ueno, Nankodo). Preferred metal ions are those of divalent transition metals, with divalent nickel, copper, zinc, cobalt, platinum and palladium being particularly preferred. The metal source compound is preferably added in an amount ranging from 0.1 to 10 moles per mole of the compound of the present invention that is incorporated in the photosensitive material. The metal source may be incorporated in the same manner as will be described below in connection with the incorporation of the compound of the present invention. For example, it is dissolvent or dispersed in a low-boiling or high-boiling point solvent and thereafter dissolved or dispersed together with the polymer for forming an image-receiving layer, and the resulting solution or dispersion is applied onto the substrate.

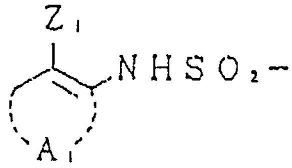
The compound of the present invention has a carrier, or a group that allows a dye compound having the dye portion to have different degrees of diffusibility as a function of silver development (i.e. said dye component has a different diffusibility after the development than before the development). This carrier is bonded to at least one of R_1, R_2, R_3, R_4, R_5 and Y.

The carrier to be used in the present invention is described hereinafter. There are two types of carriers, one being a negative type which renders the dye diffusible as a position function of silver development, and the other is a position type which renders the dye diffusible as a negative function of silver development. Carriers of the negative type are reducing carriers which are oxidized to release diffusible dyes and may be represented by the following general formulas (3) - (7):

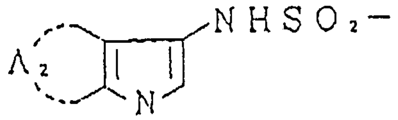
Formula (3)



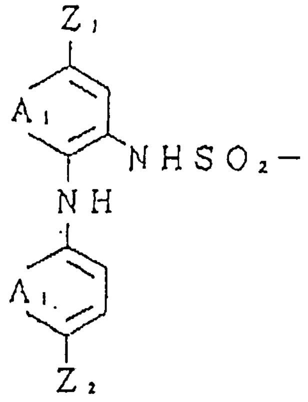
Formula (4)



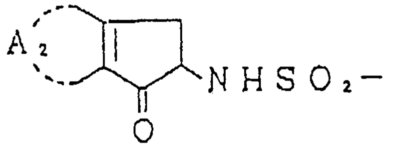
Formula (5)



Formula (6)



Formula (7)



where A_1 represents the atomic group necessary to form a benzene ring or a naphthalene ring; A_2 represents the atomic group necessary to form a condensed benzene ring; the ring formed by A_1 or A_2 may have substituents, at least one of which is a ballast group; Z_1 and Z_2 each represents a hydroxyl group, an amino group (inclusive of a substituted amino group) or a group that imparts a hydroxyl group or an amino group (inclusive of a substituted amino group) upon hydrolysis.

Specific examples of the carriers shown above are described in the specifications of prior patents such as JP-A-48-33826 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-51-113624, JP-A-57-179840, JP-A-58-116537, JP-A-59-60434, JP-A-59-65839, JP-A-59-165055, JP-A-51-104343, JP-A-59-124329, etc.

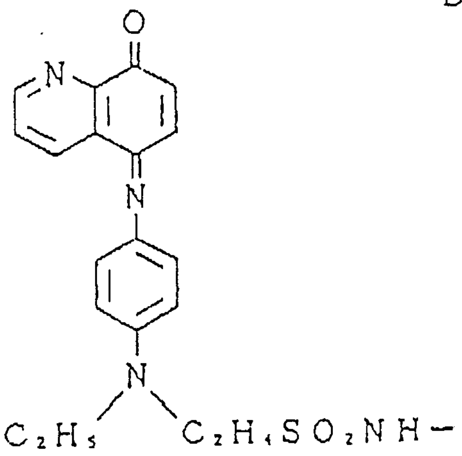
When the compound of the present invention has the carrier described above, the dye-providing material may also serve as a reducing agent. Another negative-acting carrier is a coupler residue. The dye portion is substituted at the active site of a coupler, with the coupler residue having at least one ballast group. Specific examples of carriers of this kind are described in the specifications of JP-A-57-122596, JP-A-57-186744, JP-A-59-159159, JP-A-59-174834, JP-A-59-231540, etc.

Still another negative-acting carrier is a coupler that is substituted with a ballast group at the active site, with the dye portion being substituted by a group other than at the active site. Specific examples of the carrier of this type are described in Japanese Patent Application No. 63-257998.

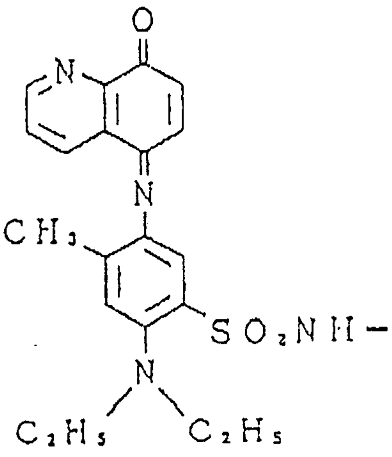
Specific examples of positive-acting carriers are described in JP-A-51-63618, JP-A-53-69033, JP-A-54-130927, JP-A-49-111628, JP-A-52-4819, JP-A-53-35533, JP-A-53-110827, JP-A-54-130927, JP-A-56-164342, and U.S. Patent No. 4,783, 396.

More specific examples of the dye portion to be used in the present invention are listed below:

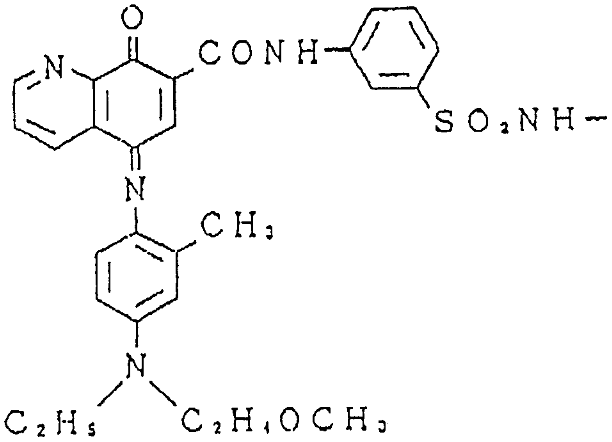
D－1



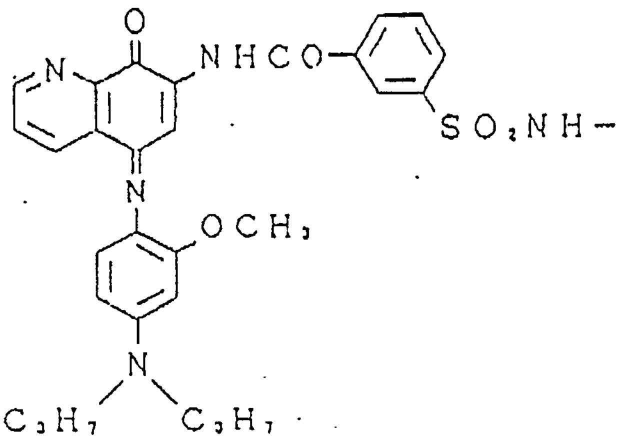
D－2



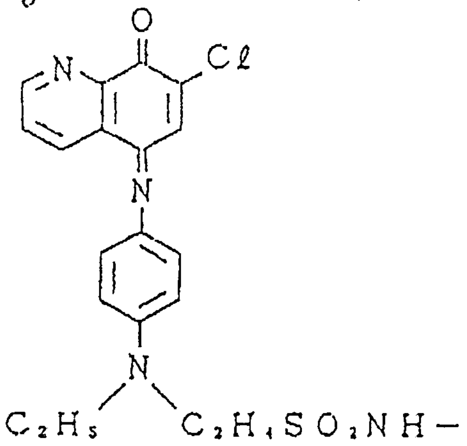
D－3



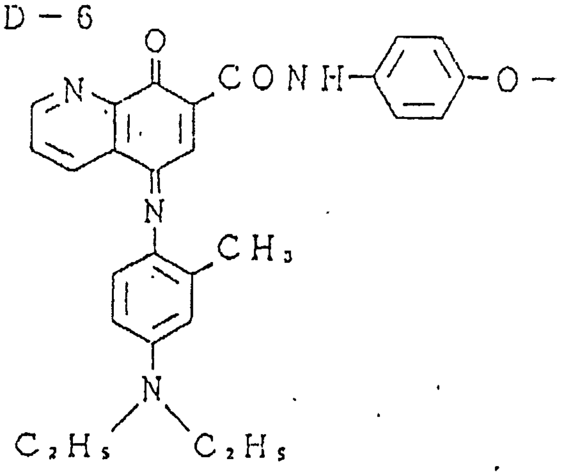
D－4



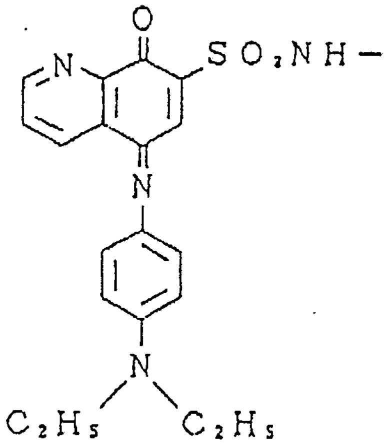
D－5



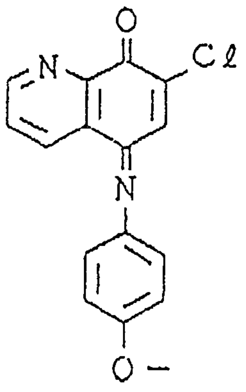
D－6



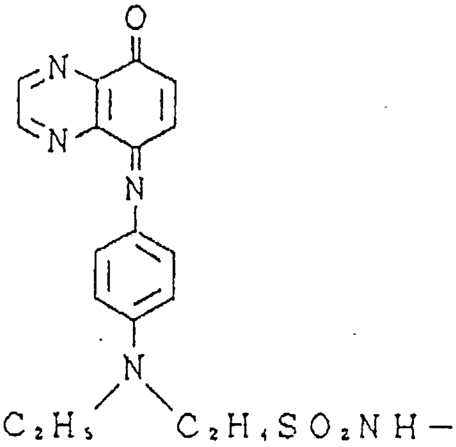
D－7



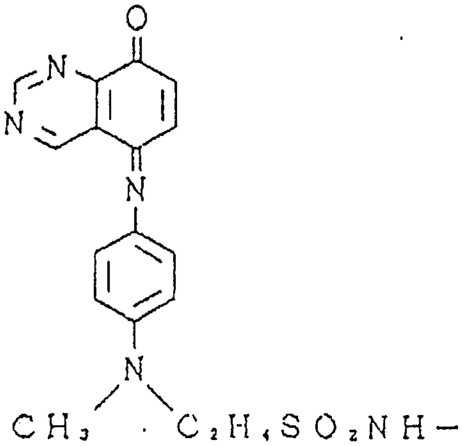
D－8



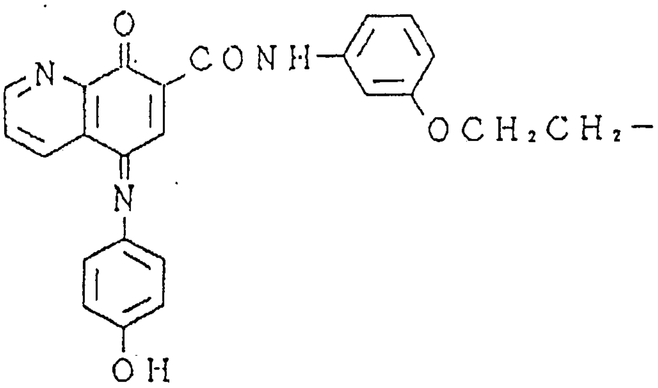
D-9



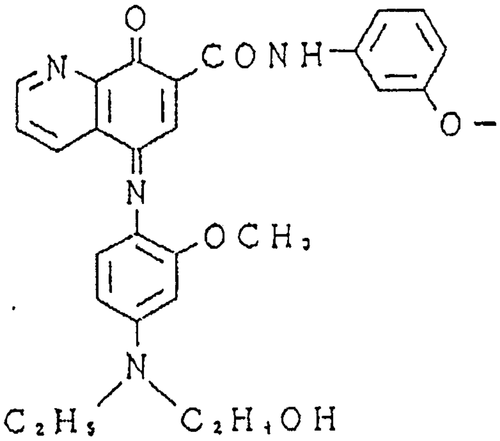
D-10



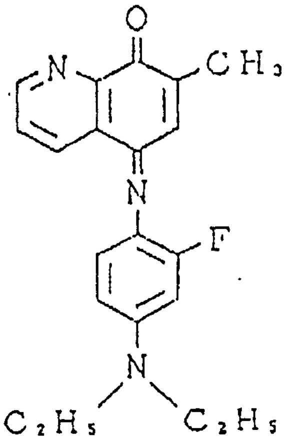
D-11



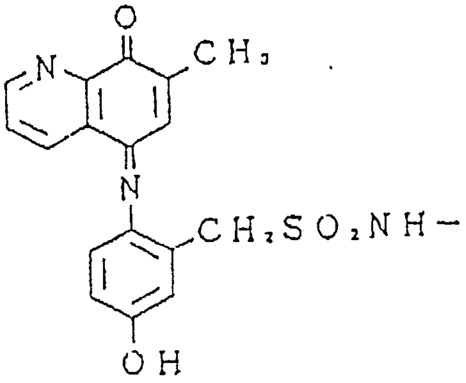
D-12



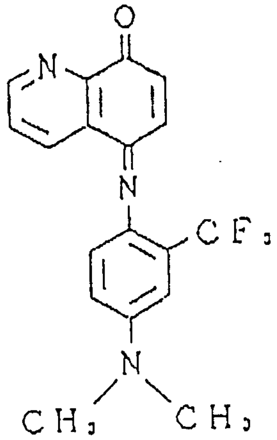
D-13



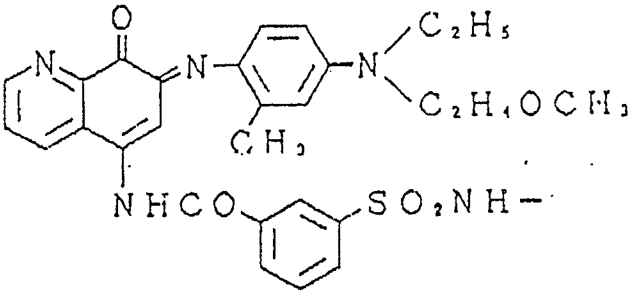
D－14



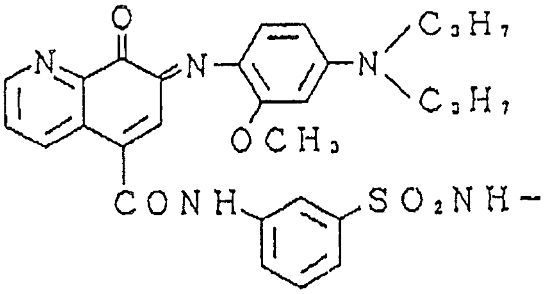
D－15



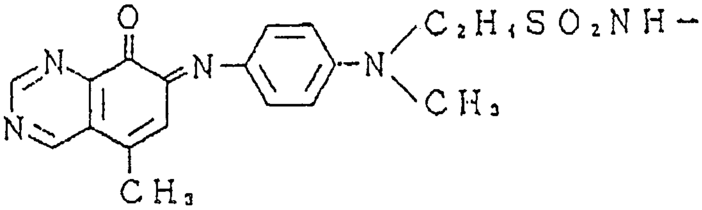
D－16



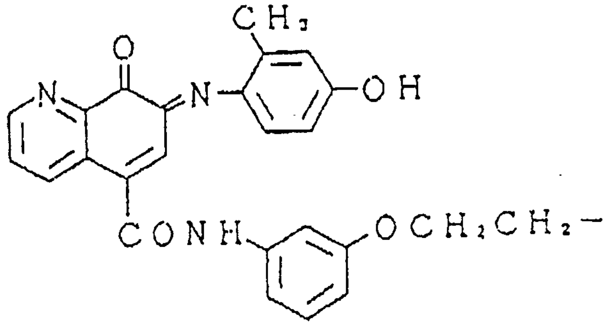
D－17



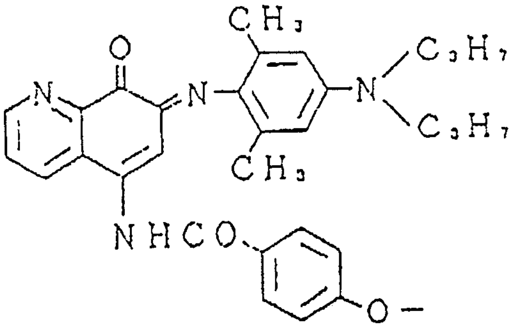
D－18



D-19

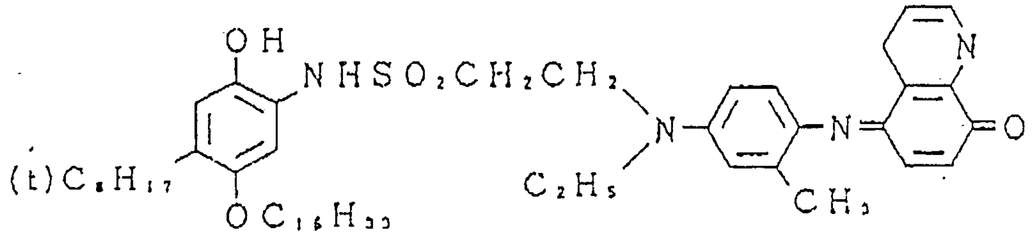


D-20



Specific examples of the compound of the present invention are listed below:

(1)



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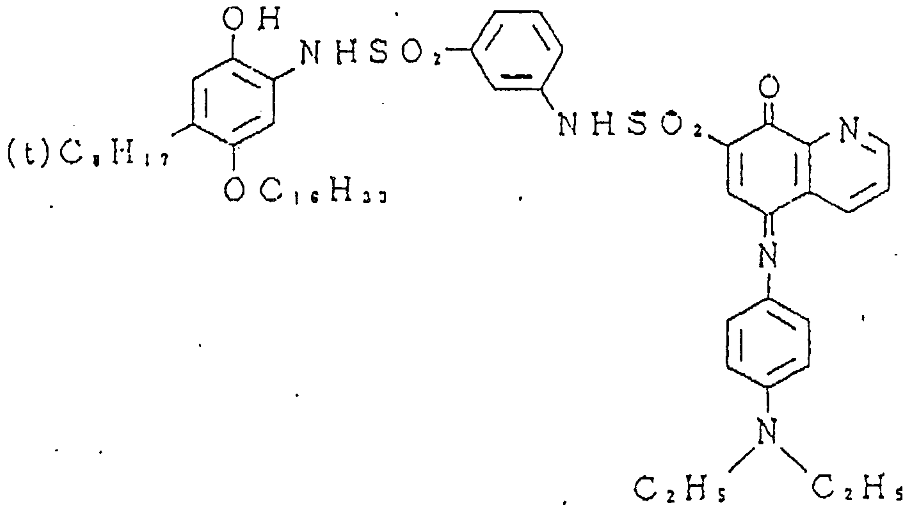

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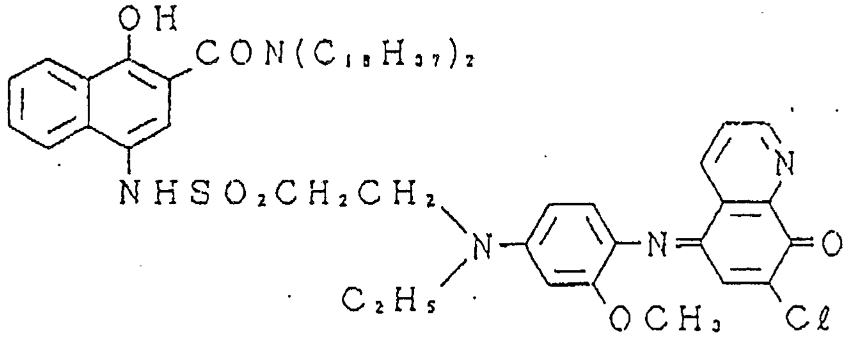

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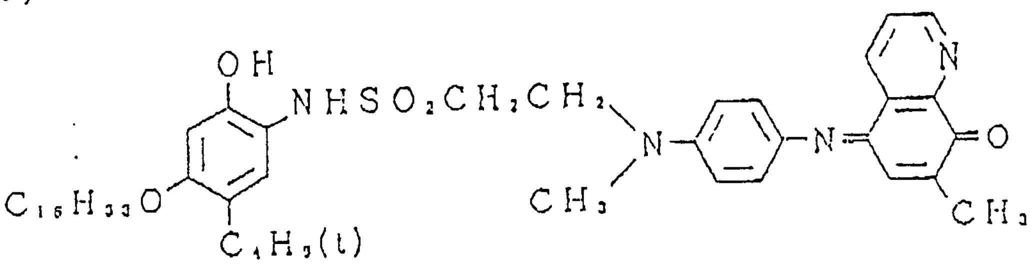
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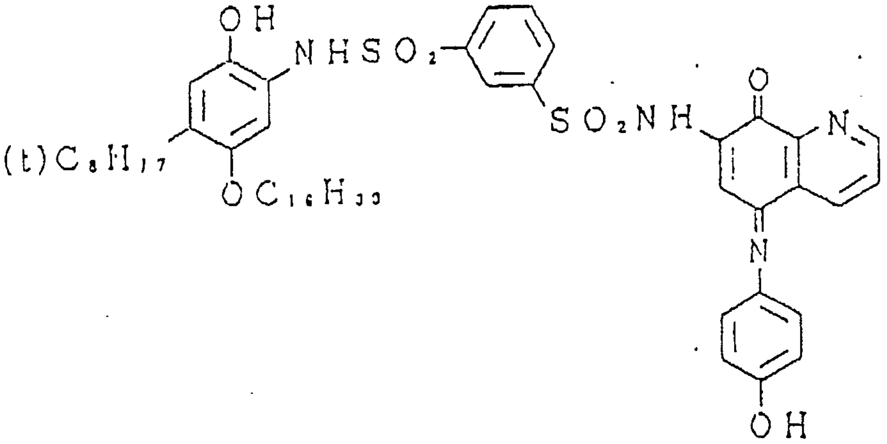
C₄H₉(t)

(5)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SO₂NH
O
N
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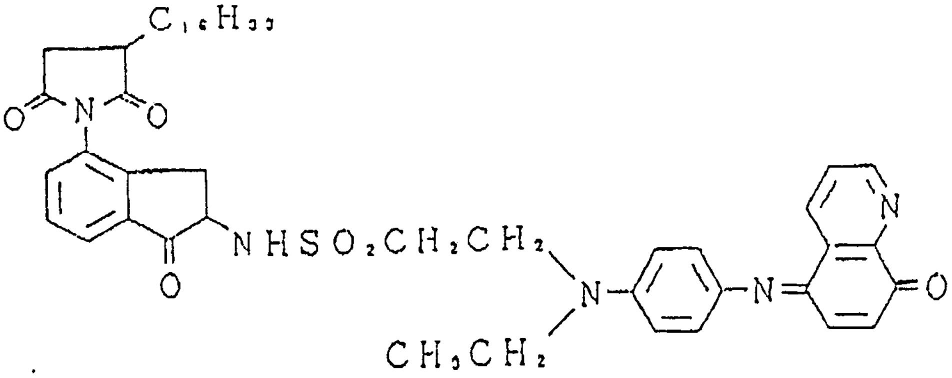
N
OH

(6)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N
O
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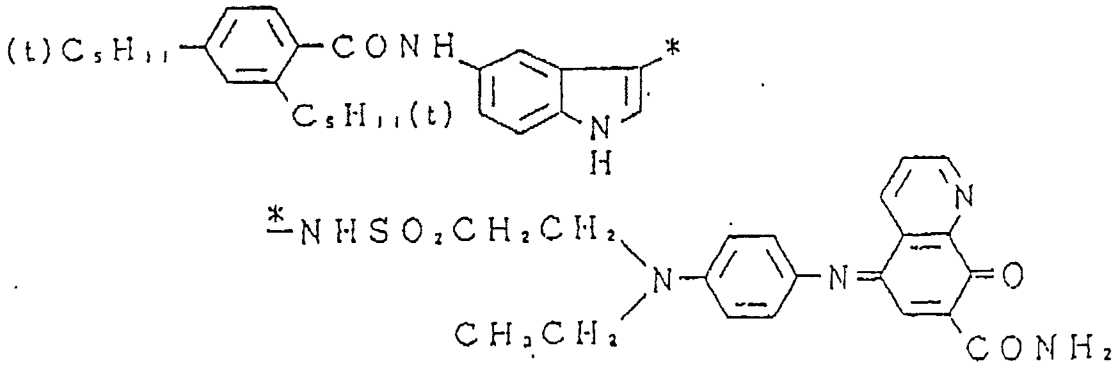
CH₃CH₂
N
N
O

(7)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H
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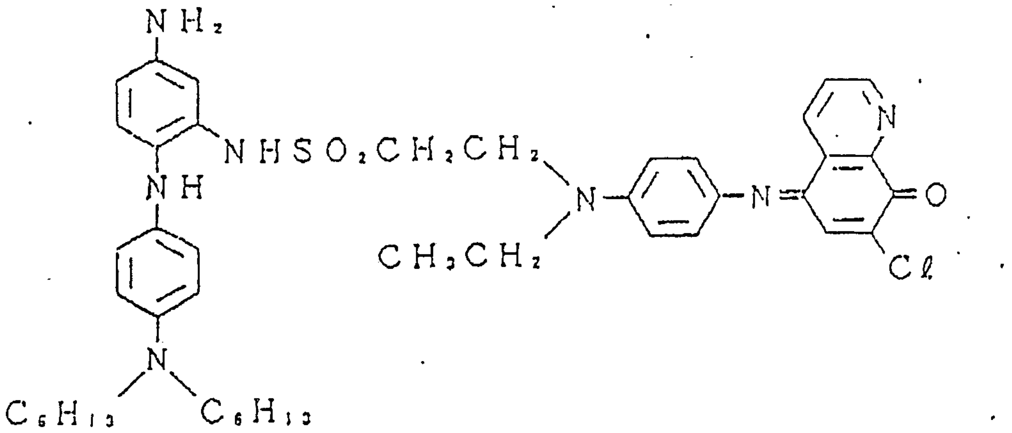
CONH₂

(8)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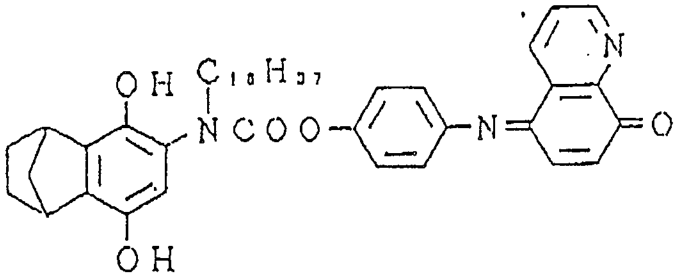
N
CH₃CH₂
N
N
O
Cℓ

(9)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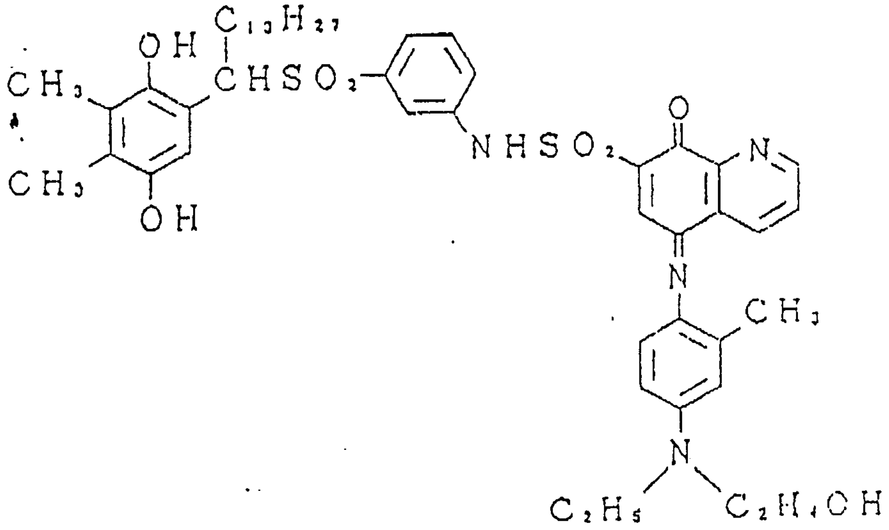
NCOO
OH
N
N
O

(10)



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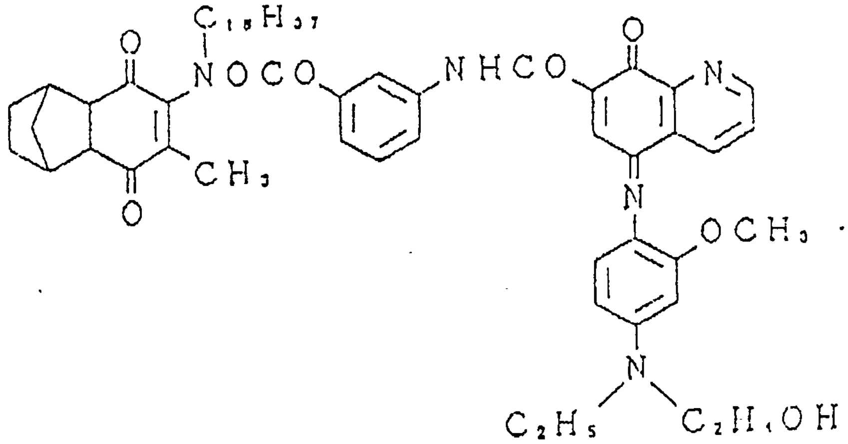

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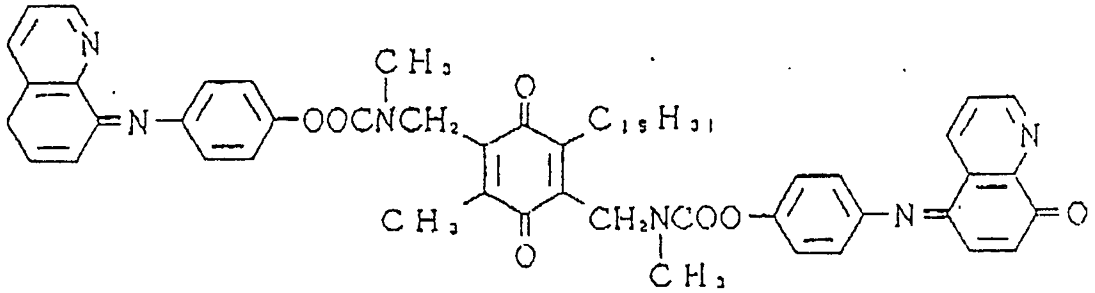

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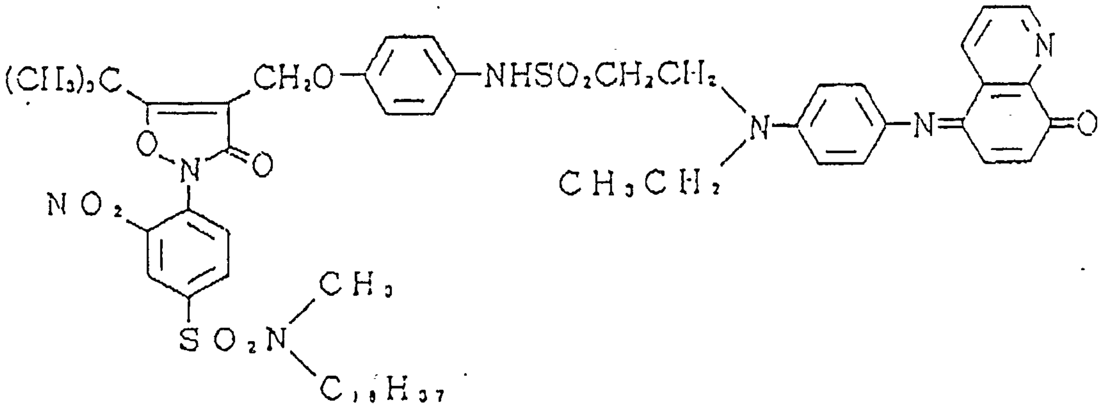

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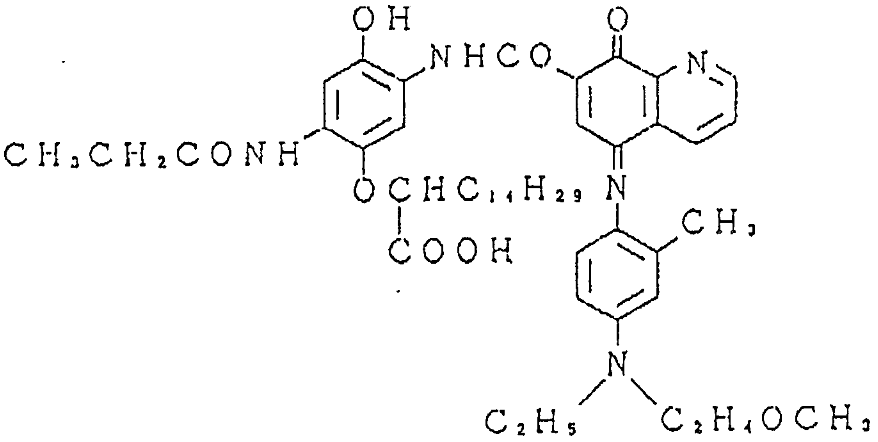

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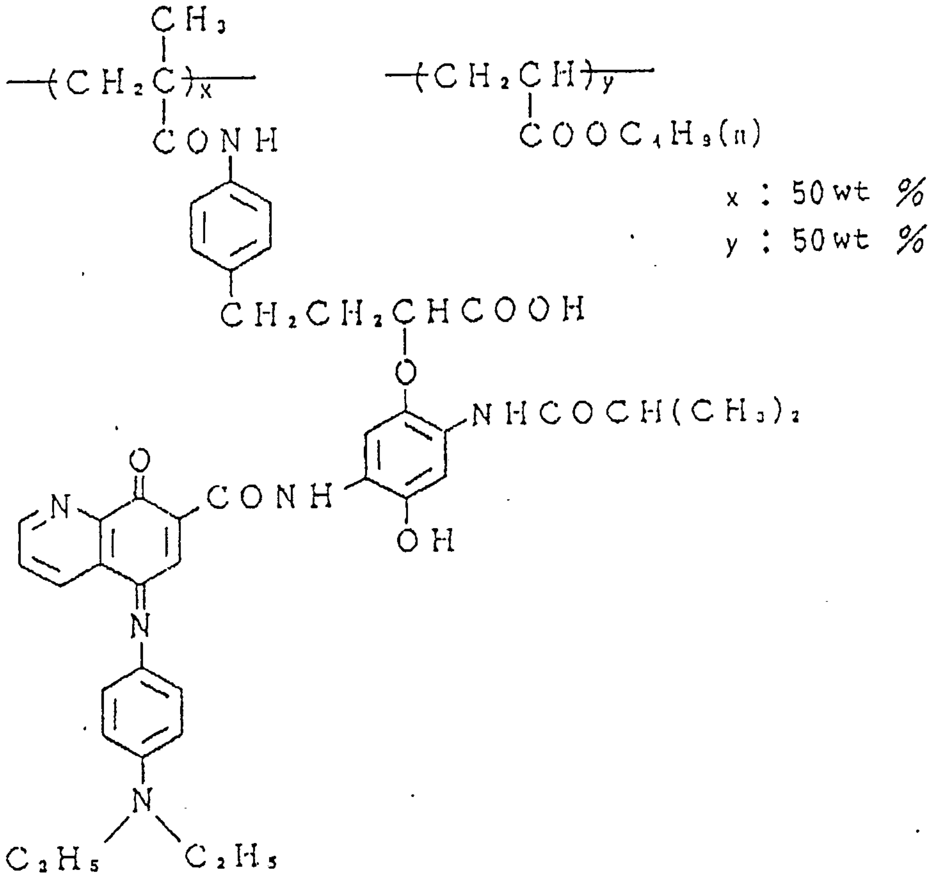
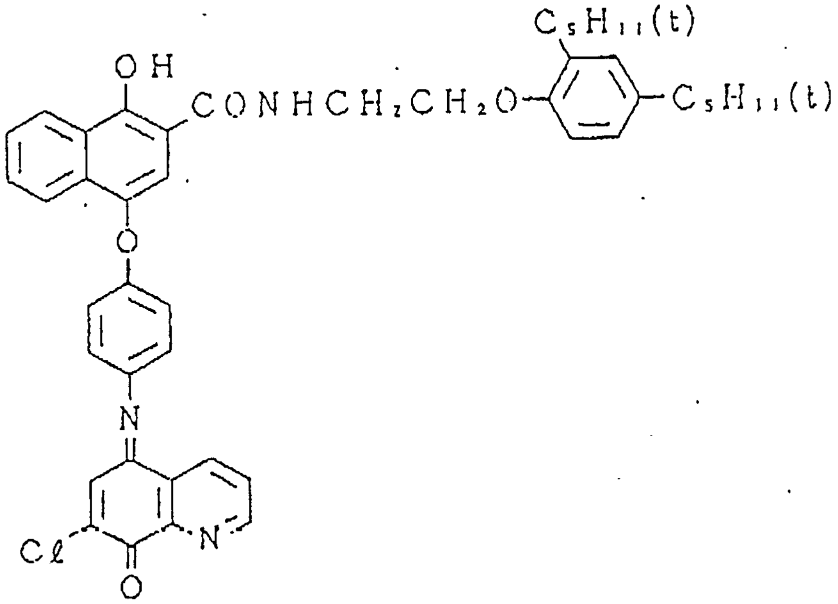

CH3
CONH
COOC4H9(n)
x : 50wt %
y : 50wt %
CH2CH2CHCOOH
O
NHCOCH(CH3)2
CONH
OH
N
O
N
N
C2H5
C2H5

(16)



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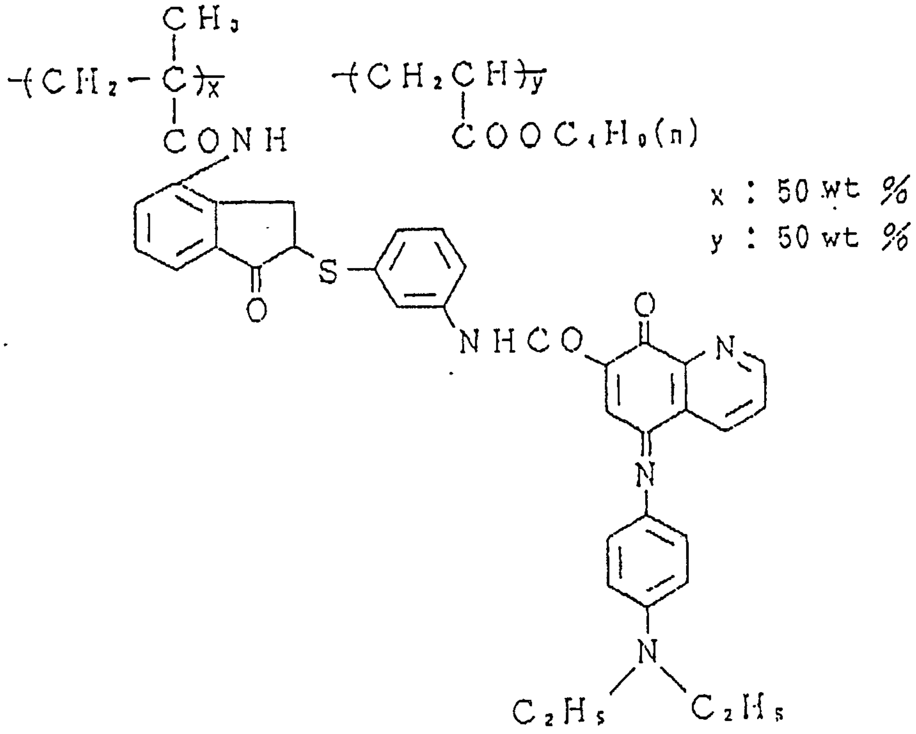
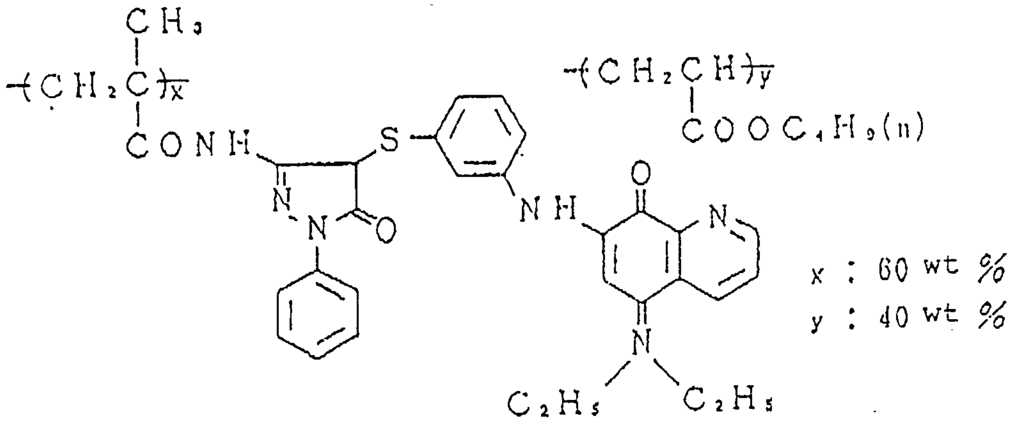


x : 50 wt %

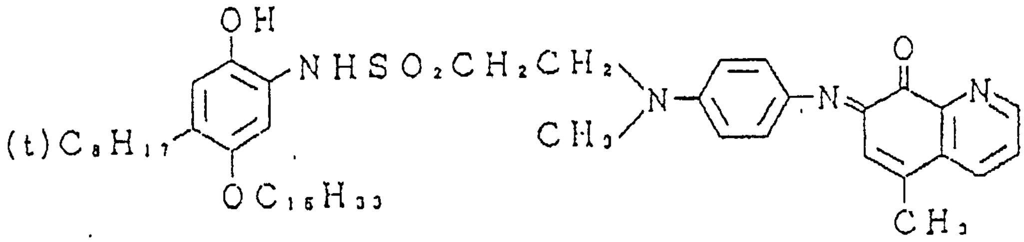
y : 50 wt %

(18)



x : 60 wt %
y : 40 wt %

(19)



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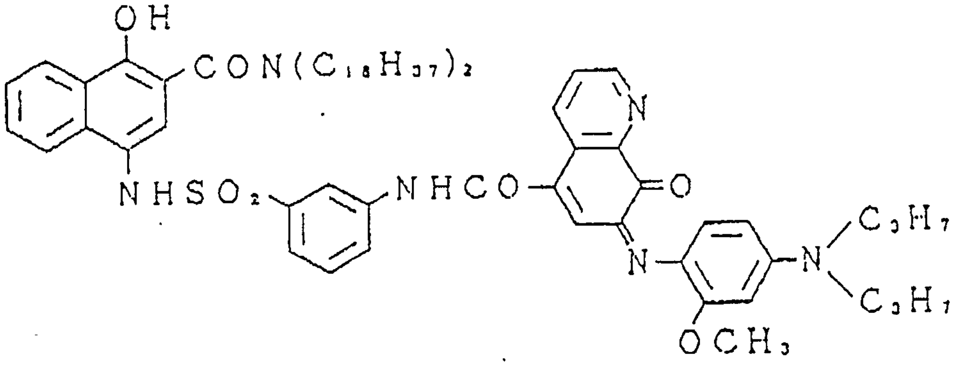
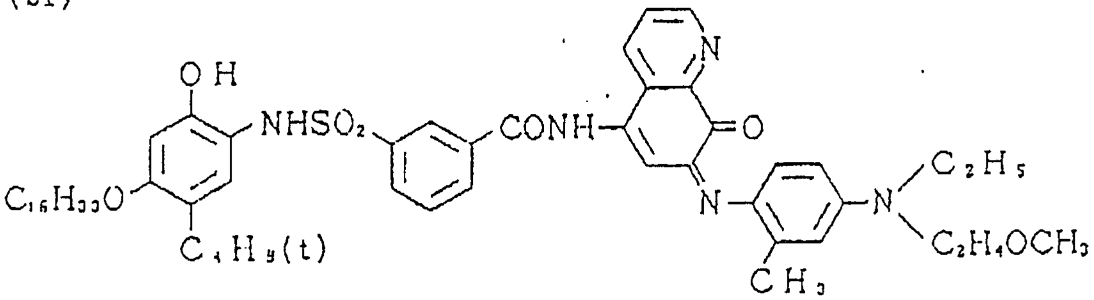
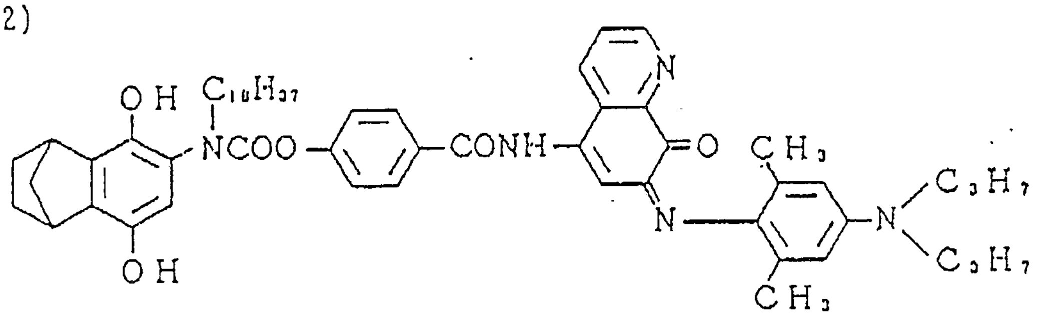


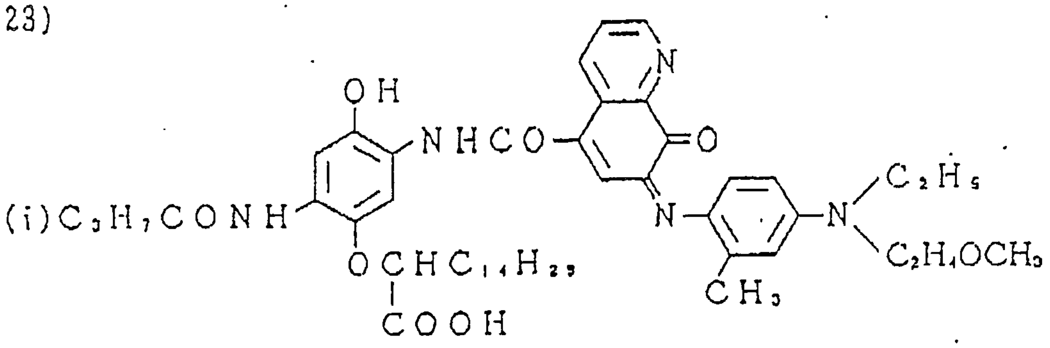
(21)


OH
NHSO₂
CONH
N
O
N
C₂H₅
C₂H₄OCH₃
C₁₆H₃₃O
C₄H₉(t)
CH₃

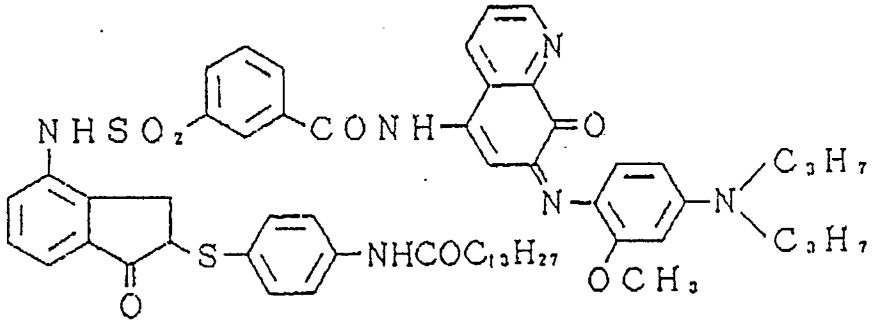
(22)


OH
C₁₈H₃₇
NCOO
CONH
N
O
CH₃
N
C₃H₇
C₃H₇
OH
CH₃

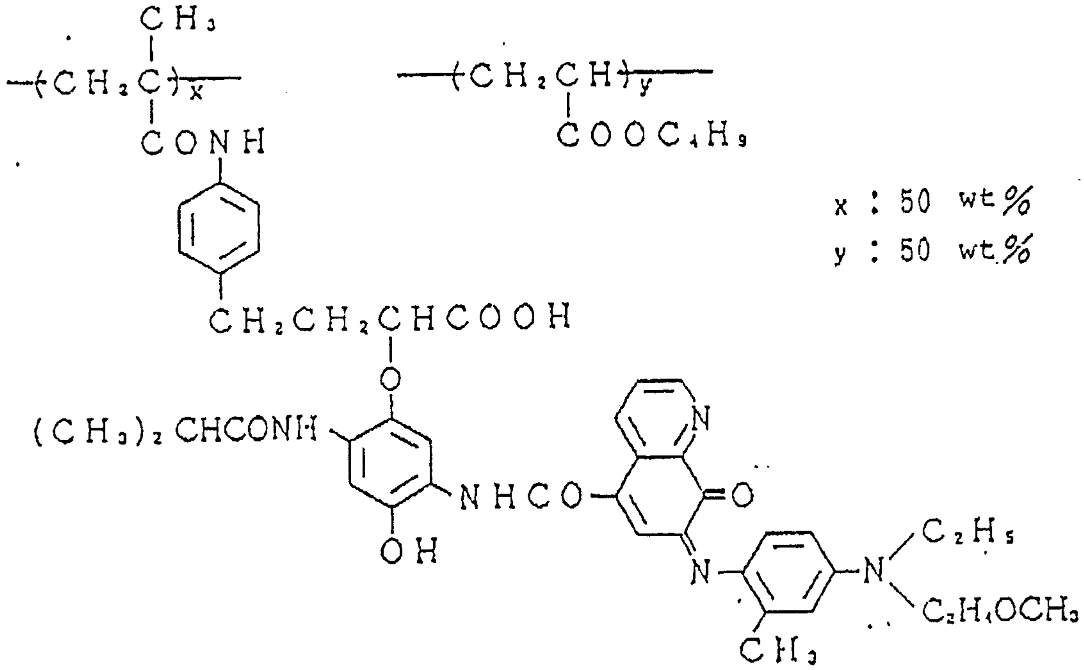
(23)


OH
NHCO
N
O
C₂H₅
(i)C₃H₇CONH
N
C₂H₄OCH₃
OCHC₁₄H₂₉
COOH
CH₃

(24)


N
NHSO₂
CONH
O
C₃H₇
N
C₃H₇
S
NHCOC₁₃H₂₇
OCH₃
O

(25)

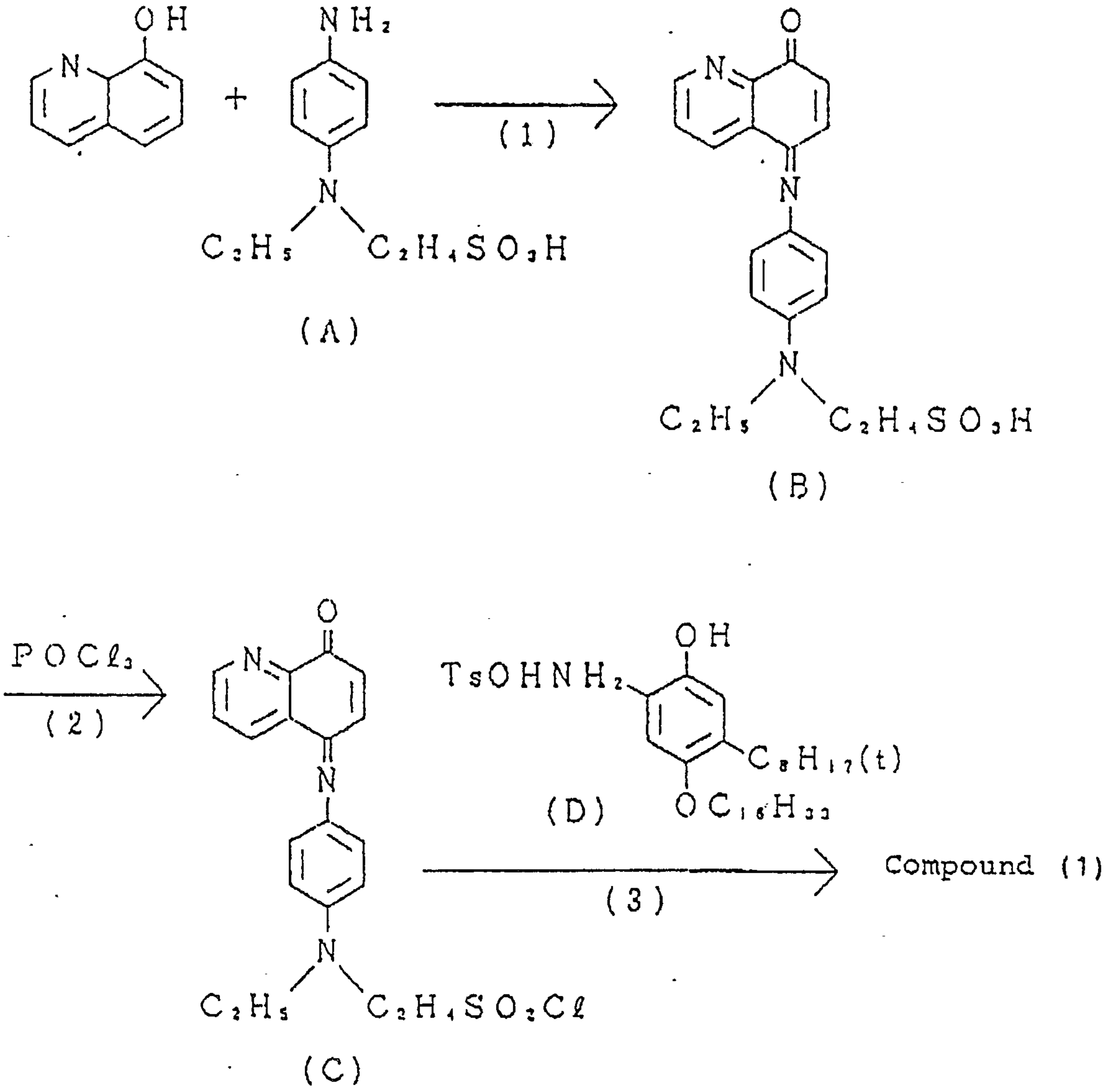


The dye portion of the compound of the present invention can be obtained by the methods described in JP-A-63-227569, Japanese Patent Application No. 62-294600. Briefly stated, it can be obtained by the oxidative coupling reaction between an 8-hydroxyquinolinol derivative and a p-phenylenediamine derivative or p-aminophenol derivative.

The compound of the present invention can also be obtained by subjecting the functional group in said dye portion to reaction, say condensation reaction, with the carrier portion either directly or after it is converted to an acid chloride (e.g. sulfonyl chloride).

The compound of the present invention can also be synthesized by first reacting an 8-hydroxyquinolinol derivative with the carrier portion and then subjecting the reaction product to oxidative coupling.

A specific method of synthesizing the compound of the present invention is described below, with illustrative compound (1) taken as an example. This compound (1) may be synthesized by the following scheme:



Step (1):

Ten grams of compound (A) is dissolved in 1.5 L of ice water and 2.6 g of sodium carbonate and 2.5 g of sodium hydroxide are added. To the stirred mixture, 200 ml of an aqueous solution containing 3 g of 8-hydroxyquinoline and 1.5 g of sodium hydroxide are added. Thereafter, 62 ml of 5% sodium hypo-chlorite is added dropwise at 5° C. The resulting precipitate is separated by filtration and purified by column chromatography to obtain compound (B).

Step (2):

Compound (B) (7.7 g) is dissolved in 100 ml or dimethylformamide and 6 ml of phosphorus oxychloride is added dropwise at 15 - 20° C. Following stirring at 40 -45° C for an additional 2 h, the solution is poouredinto ice water. The precipitating blue crystal is separated by filtration and dried with the air to obtain compound (C).

Step (3):

With nitrogen gas being passed through a mixture of compound (D) (7.5 g), pyridine (7.5 ml) and dimethylformamide (40 ml), 4.84 g of compound (C)1 is added in small portions. Following stirring at room temperature for 1 hr, the reaction solution is poured into dilute HCl and the mixture is subjected to extraction with ethyl acetate. The ethyl acetate layer is separated, dried and concentrated. The solid cake is purified by column chromatography to obtain compound (1) of the present invention. When put into chloroform, this compound has a visible spectram with λmax at 625 nm (ε: 18,000).

The compounds of the present invention described above may be used either independently or as admixtures. The amount of these compounds used is by no means critical and may be determined according to their type, the manner in which they are used (i.e., either singly or in combination) or the number of photographic constituent layers of which the light-sensitive material of the present invention is composed (i.e., a single layer or two or more layers in superposition). As a guide, the compounds may be used in an amount of 0.005 - 50 g, preferably 0.1 - 10 g, per square meter.

The compounds of the present invention may be incorporated in photographic constituent layers in a heat-processible color photosensitive material by any suitable method. For instance,they are dissolved in low-boiling solvents (e.g., methanol, ethanol and ethyl acetate) and/or high-boiling solvents (e.g., dibutyl phahlate, dioctyl phthalate and tricresyl phosphate) and uniform dispersions are made. Alternatively, the dye compounds are dissolved in alkaline aqueous solutions (e.g., a 10% aqueous solution of sodium hydroxide) and neutralized with acids (e.g., citric acid or nitric acid). In another method, the compounds are dispersed in solid form in aqueous solutions of appropriate polymers (e.g., gelatin, polyvinylbutyral and polyvinylpyrrolidone).

Light-sensitive silver halides that can be used in the present invention include silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chloroiodido, silver iodobromide, etc. These light-sensitive silver halides can be prepared by any of the methods commonly employed in the photographic art.

If desired, a silver halide emulsion having silver halide grains with a duplex structure (i.e., the halide composition of the grain surface differing from that of the interior) may be used and an example of such duplex grains is core/shell type silver halide grains. The shell of these grains may change in halide composition stepwise or gradually. The silver halide grains used may have a well-defined crystal habit as in cubes, spheres, octahedra, dodecahedra or tetradecahedra. Alternatively, they may not have any well-defined crystal habit. Illustrative silver halides of this type are shown in JP-A-60-215948.

A silver halide emulsion comprising tabular silver halide grains of the type described in JP-A-58-111933, JP-A-58-111934, JP-A-58-108526 and Research Disclosure No. 22534 may also be used; such grains have two parallel crystal planes each of which has a greater area than any other single crystal of these grains and the aspect ratio (i.e., diameter-to-thickness ratio) of these grains is at least 5:1.

The present invention also permits the use of a silver halide emulsion containing internal latent-image forming silver halide grains whose surface is not prefogged. Examples of such emulsions include: those which comprise silver halide grains having a higher sensitivity in their interior than on the surface, as shown in USP 2,592,250, 3,206,313, 3,327,322, 3,511,622, 3,447,927, 3,761,266, 3,703,584 and 3,746,140; those which comprise silver halide grains having polyvalent metal ions incorporated therein, as shown in USP 3,271,157, 3,447,927 and 3,531,291; those which comprise dopant-containing silver halide grains with their surface being chemically sensitized by a small extent, as shown in USP 3,761,276; those which comprise grains with a multi-layered structure, as shown in JP-A-50-8254 and JP-A-50-38525; and silver halide emulsions of the type described in JP-A-52-156614 and JP-A-55-127549.

The silver halide grains in these light-sensitive emulsions may be course or fine; preferred grain sizes are in the order of 0.005 μm to 1,5 μm in diameter, with the range of from about 0.01 to about 0.5 μm being more preferred.

According to another method for preparing light-sensitive silver halides, a light-sensitive silver salt forming component may be used in the presence of organic silver salts (to be described below) so as to form light-sensitive silver halides in part of the organic silver salts.

These light-sensitive silver halides and light-sensitive silver salt forming component may be used in combination in a variety of methods, and the amount used in one photographic layer preferably ranges from 0.001 to 50 g, more preferably 0.1 - 10 g, per square meter of support.

The light-sensitive silver halide emulsions illustrated above may be chemically sensitized by any of the methods commonly employed in the photographic art.

The light-sensitive silver halide emulsion used in the present invention may be spectrally sensitized with known spectral sensitizing dyes to provide sensitivity to blue, green, red or infrared light.

Typical examples of the spectral sensitizing dyes that can be used in the present invention include cyanine dyes, merocyanine dyes, complex (tri- or tetra-nuclear) cyanine dyes, holopolar cyanine dyes, styryl dyes, hemicyanine dyes and oxonole dyes.

These sensitizing dyes are incorporated in amounts ranging from 1 x 10^{-6} to 1 mole, preferably from 1 x 10^{-5} to 1 x 10^{-1} mole, per mole of the light-sensitive silver halide or silver halide forming component.

The sensitizing dyes may be added at any stage of the preparation of silver halide emulsions; namely, they may be added at any stage such as during the formation of silver halide grains, during the removal of soluble salts, prior to the start of chemical sensitization, during chemical sensitization, or after completion of chemical sensitization.

The reducing agent to be used in the heat-processible color photosensitive material of the present (the term "reducing agent" as used herein shall include precursors of the reducing agent) may be selected from among these which are commonly used in the field of heat-processible photosensitive materials.

Reducing agents that can be used in the present invention are described in, for example, USP 3,531,286, 3,761,270, 3,764,328, Research Disclosure Nos. 12146, 15108 and 15127, JP-A-56-27132, USP 3,342,599, 3,719,492, JP-A-53-135628 and JP-A-57-79035, and they include: p-phenylenediamino and p-aminophenolic developing agents, phosphoroamidophenolic and sulfonamidoaniline based developing agents, hydrazone based color developing agents, and precursors thereof, as well as phenols, sulfonamidophenols, polyhydroxybenzenes, naphthols, hydroxybinaphthyls, methylenebisnaphthols, methylenebisphenols, ascorbic acids, 3-pyrazolidones and pyrazolones.

Dye-providing materials may themselves serve as reducing agents.

Particularly preferred reducing agents are N-(p-N,N-dialkylamino) phenylsulfamic acid salts as described in JP-A-56-146133 and JP-A-62-727141.

The reducing agents described above may be used either independently or as admixtures.

The amount in which the reducing agents are used in the heat-processible color photographic material of the present invention depend upon many factors such as the type of light-sensitive silver halide used, the type of organic silver salt, and the type of other additives used. Usually, the reducing agents are used in amounts ranging from 0.01 to 1,500 moles, more preferably from 0.1 to 200 moles, per mole of the light-sensitive silver halide.

Illustrative binders that can be employed in the heat-processible color photosensitive material of the present invention include: synthetic high-molecular compounds such as polyvinylbutyral, polyvinyl acetate, ethyl collulose, polymethyl methacrylate, cellulose acetate butyrate, polyvinyl alcohol and polyvinylpyrrolidone; synthetic or natural high-molecular compounds such as gelatin, gelatin derivatives (e.g., phthalated gelatin), cellulose derivatives, proteins, starches, and gum arabic. These high-molecular compounds may be used either singly or in combination. It is particularly preferred to employ gelatin or its derivatives in combination with hydrophilic polymers such as polyvinylpyrrolidone and polyvinyl alcohol. A more preferred binder is a mixture of gelatin and polyvinylpyrrolidone as disclosed in JP-A-59-229556.

The binders are generally used in amounts ranging from 0.05 to 50 g, preferably from 0.2 to 20 g, per square meter of a support.

The binders are preferably used in amounts of 0.1 -10 g, more preferably 0.2 - 5 g, per gram of the dye-providing material.

The color light-sensitive material of the present invention may contain not only the compound of the present invention but also other dye-providing materials. Examples of such optionally used dye-providing materials include couplers capable of forming non-diffusible dyes as described in JP-A-62-44737, JP-A-62-129852 and JP-A-62-169158, leuco dyes as described in USP 475,441, and azo dyes for use in a heat development dye bleaching method as described in USP 4,235,957. More preferably, diffusion-type dye-providing materials which are capable of forming or releasing diffusible dyes are used, and it is particularly preferred to use compounds that form diffusible dyes by coupling reaction.

Any diffusion-type dye-providing materials can be used as long as they are capable of forming or releasing diffusible dyes as a function of the reduction reaction of light-sensitive silver halides and/or optionally used organic silver salts, and depending on the type of reaction involved, such dye-providing materials are classified as negative-acting dye-providing materials and positive-acting dye-providing materials.

Illustrative negative-acting dye-providing materials are reducing dye-releasing compounds of the types described in USP 4,463,079, 4,439,513, JP-A-59-60434, JP-A-59-65839, JP-A-59-71046, JP-A-59-87450, JP-A-59-88730, JP-A-59-123837, JP-A-59-124329, JP-A-59-165054, JP-A-59-164055, etc.

Other negative-acting dye-providing materials are coupling dye-releasing compounds of the types described in USP 4,474,867, JP-A-59-12431, JP-A-59-48765, JP-A-59-174834, JP-A-59-776642, JP-A-59-159159, JP-A-59-231040, etc.

Coupling dye-forming compounds which are particularly preferred negative-acting dye-providing materials are represented by the following general formula (A):

$\mathrm{CO} (J) (B)$ (A)

where Cp represents an organic group (coupler residue) capable of entering into reaction (coupling reaction) with the oxidation product of a reducing agent to form a diffusible dye; J represents a divalent linkage group bound to the active site reacting with the oxidation product of a reducing agent; and B is a ballast group. The ballast group renders the dye-providing material to be substantially non-diffusible during heat development and it may exhibit this action on account of either its molecular nature (as in a sulfo group) or its size (as in a group having a large number of carbon atoms). In order to insure the formation of a highly diffusible dye, the coupler residue represented by Cp preferably has a molecular weight of no higher than 700, more preferably no higher than 500.

The ballast group preferably has at least 8 carbon atoms, more preferably at least 12 carbon atoms, and a group comprising a polymer chain is particularly preferred.

A preferred example of the coupling dye-forming compound having a polymer-chain group is such that said group is composed of a polymer chain having recurring units derived from a monomer represented by the following general formula (B):

$\mathrm{Co} (J) (Y)_{\ell} (Z) (L)$ (B)

where Cp and J are the same as defined in the general formula (A); Y is an alkylene, arylene or aralkylene group; ℓ is 0 or 1; Z is a divalent organic group; and L is an ethylenically unsaturated group or a group having an ethylenically unsaturated group.

Specific examples of the coupling dye-forming compounds represented by the general formulas (A) and (B) include those which are described in JP-A-59-124339, JP-A-50-181345, JP-A-60-2950, JP-A-61-57943, JP-A-61-59336, USP 4,631,251, 4,650,748, 4,656,124, etc. Particularly preferred are polymer-type dye-providing materials as described in USP 4,656,124, 4,631,251 and 4,650,748.

Exemplary positive-acting dye-providing materials include compounds of the types described in JP-A-59-55430, JP-A-59-165054, JP-A-154445, JP-A-59-766954, JP-A-59-116655, JP-A-59-124327, JP-A-59-152440, etc.

These dye-providing materials may be used either on their own or as admixtures. The amounts of their use is by no means critical and may be determined according to their type, the manner in which they are used (i.e. either singly or in combination) or the number of photographic constituent layers of which the light-sensitive material of the present invention is composed (i.e., a single layer or two or more layers in superposition). As a guide, these dye-providing materials may be used in an amount of 0.005 -50 g, preferably 0.1 - 10 g, per square meter.

The dye-providing materials to be used in the present invention may be incorporated in photographic constituent layers in a heat-processible color photosensitive material by any suitable method. For instance, they are dissolved in a low-boiling solvent (e.g. methanol, ethanol or ethyl acetate) and/or a high-boiling solvent (e.g. dibutyl phthalate, dioctyl phthalate or tricresyl phosphate) and uniform dispersions are made. Alternatively, the dye-providing materials are dissolved in alkaline aqueous solutions (e.g. a 10% aqueous solution of sodium hydroxide) and neutralized with acids (e.g. citric acid or nitric acid). In another method, the dye-providing materials are dispersed in solid form in aqueous solutions of appropriate polymers (e.g., gelatin, polyvinylbutyral and polyvinylpyrrolidone).

A variety of organic silver salts may optionally be employed in the heat-processible color photosensitive material of the present invention in order to increase its sensitivity or improve its developability.

Illustrative organic silver salts that may be employed in the heat-processible color photosensitive material of the present invention include: silver salts of long-chain aliphatic carboxylic acids and silver salts of carboxylic acids having a hetero ring, such as silver behenate and silver α-(1-phenyltetrazolethio)acetate (see JP-A-53-4921, JP-A-49-52626, JP-A-52-141222, JP-A-53-36224, JP-A-53-37626, JP-A-53-37610, USP 3,330,633, 3,794,496 and 4,105,451); and silver salts of an imino group as described in Japanese Patent Publication Nos. JP-A-44-26582, 45- 12700, 45-18416, 45-22185, JO-A-52-137321; JP-A-58-118638, JP-A-58-118639, and USP 4,123,274.

Among the organic silver salts listed above, silver salts of an imino group are preferred. Particularly preferred are silver salts of benzotriazole derivatives such as 5-methylbenzotriazole or derivatives thereof, sulfobenzotriazole or derivatives thereof and N-alkylsulfamoylbenzotriazole or derivatives thereof.

These organic silver salts may be used either singly or as admixtures in the present invention. Silver salts prepared in suitable binders may be immediately used without being isolated. Alternatively, isolated silver salts may be dispersed in binders by suitable means before they are used. Methods of obtaining dispersions are illustrated by, but are in no way limited, to a ball mill, a sand mill a vibration mill, etc.

The organic silver salts are preferably used in amounts ranging from 0.01 to 500 moles, more preferably from 0.1 to 100 moles, most preferably from 0.3 to 30 moles, per mole of the light-sensitive silver halide.

In the heat-processible color photosensitive material of the present invention and if this material is of the transfer type and used with an image-receiving member, a variety of thermal solvents are preferably incorporated in the light-sensitive material and/or the image-receiving member. Thermal solvents usable in the present invention are compounds that are liquid during thermal development and that promote thermal development and/or heat transfer. Examples of such compounds are the polar organic compounds that are described in USP 3,347,675, 3,667,959, Research Disclosure No. 17643 (XII), JP-A-59-229556, JP-A-59-68730, JP-A-59-84236, JP-A-60-191251, JP-A-60-232547, JP-A-60-14241, JP-A-61-52643, JP-A-62-78554, JP-A-62-42153, JP-A-62-44737, USP 3,438,776, 3,666,477, 3,667,959, JP-A-51-19525, JP-A-53-24829, JP-A-53-60223, JP-A-58-118640, and JP-A-58-198038. Particularly useful compounds are: urea derivatives (e.g., dimethylurea, diethylurea and phenylurea), amide derivatives (e.g., acetamide, benzamide and p-toluamide), sulfonamide derivatives (e.g., benzenesulfonamide and α-toluenesulfonamide), and polyhydric alcohols (e.g., 1,6-hexanediol, 1,2-cyclohexanediol and pentaerythritol, and polyethylene glycol.

Among these thermal solvents, water-insoluble solid thermal solvents may be used with particular advantage.

Specific examples of such water-insoluble thermal solvents are given in JP-A-62-136645, JP-A-62-139549, JP-A-63-53548, as well as Japanese Patent Application Nos. 63-205288 and 63-54113.

Thermal solvents may be incorporated in various layers such as light-sensitive silver halide emulsion layers, intermediate layers, protective layers, and image-receiving layers in an image-receiving member so that the results desired in respective cases can be obtained.

Thermal solvents are usually incorporated in amounts ranging from 10 to 500 wt%, preferably from 30 to 200 wt%, of the binder.

Organic silver salts and thermal solvents may be dispersed in the same dispersion. The binder, dispersion medium and disperser to be employed in this case may be the same as those used in preparing dispersions of the individual components.

Besides the components described above, the heat-processible color photosensitive material of the present invention may incorporate various other additives such as a development accelerator, an antifoggant and a base precursor. Useful development accelerators include the compounds described in JP-A-59-177550, JP-A-59-111636 and JP-A-59-124333, the development accelerator releasing compounds described in JP-A-61-159642 and Japanese Patent Application No. 62-203908, and the metallic ion having an electronegativity of 4 or more as described in Japanese Patent Application No. 63-104645. Illustrative antifoggants include: the higher aliphatic compound described in USP 3,645,739; the mercuric salt described in Japanese Patent Publication No. 47-11113; the N-halogen compound described in JP-A-51-47419; the mercapto compound releasing compounds described in USP 3,700,457 and JP-A-51-50725; the arylsulfonic acid described in JP-A-49-125016; the lithium salt of a carboxylic acid described in JP-A-51-47419; the oxidizing agents described in BP 1,455,271 and JP-A-50-101019; the sulfinic acids or thiosulfonic acids described in JP-A-53-19825; 2-thiouracils described in JP-A-51-3223; the elemental sulfur described in JP-A-51-26019; the disulfide and polysulfide compounds described in JP-A-51-42529, JP-A-51-81124 and JP-A-55-93149; the rosin or diterpenes described in Japanese JP-A-51-57435; polymeric acids having a free carboxylic or sulfonic acid group as described in JP-A-51-104338; the thiazolinethione described in USP 4,138,265; the 1,2,4-triazole or 5-mercapto-1,2,4-triazole described in JP-A-54-51821 and USP 4,137,079; the thiosulfinic acid esters described in JP-A-55-140833; the 1,2,3,4-thiatriazoles described in JP-A-55-142331; the dihalogen or trihalogen compounds described in JP-A-59-46641, JP-A-59-57233 and JP-A-59-57234; the thiol compound described in JP-A-59-111636; the hydroquinone derivative described in JP-A-60-198540; and the use of hydroquinone and benzotriazole derivatives as shown in JP-A-60-227255.

Other preferred antifoggants include the restrainer having a hydroxyl group that is described in JP-A-62-78554, the polymeric restrainer described in JP-A-62-121452, and the restrainer compound having a ballast group that is described in JP-A-62-123456.

The colorless coupler described in Japanese Patent Application No. 62-320599 is another anti-foggant that is preferably used.

Illustrative base precursors include compounds that undergo decarboxylation upon heating to release a basic substance (e.g., guanidium trichloroacetate) and compounds that are decomposed by reactions such as intramolecular nucleophilic substitution reaction to release amines. Examples of such base releasers are described in many prior patents such as JP-A-56-130745, JP-A-56-132332, BP 2,079,480, USP 4,060,420, JP-A-59-157637; JP-A-59-166943, JP-A-59-180537, JP-A-59-174830, JP-A-59-195237, JP-A-62-108249, and JP-A-62-174745.

Other additives may also be incorporated in the heat-processible color photosensitive material of the present invention. Illustrative additives include anti-halation dyes, brighteners, hardeners, antistats, plasticizers, extenders, matting agents, surface-active agents and anti-fading agents. Specific examples are given in

Research Disclosure, Vol. 170, No. 17029, June 1978, and JP-A-62-135825.

These various additives may be incorporated not only in the light-sensitive layers but also in non-light-sensitive layers such as an intermediate layer, a protective layer and a backing layer.

The heat-processible color photosensitive material of the present invention comprises (a) a light-sensitive silver halide, (b) a reducing agent, (c) a binder and (d) a dye-providing material. If necessary, (e) an organic silver salt is preferably contained. Basically, these components may be contained in one thermally developable light-sensitive layer but they are not necessarily incorporated in a single photographic constituent layer and may be incorporated in two thermally developable light-sensitive layers, with (a), (b), (c) and (e) being contained in one thermally developable light-sensitive layer and the dye-providing material (d) contained in the adjacent other layer. If necessary, these components may be incorporated in more than two constituent layers in such a way that they are held mutually reactive.

If desired, the thermally developable light-sensitive layer may be divided into two or more layers including a highly sensitive layer and a less sensitive layer, or a high-density layer and a low-density layer.

The thermally developable light-sensitive material of the present invention has one or more thermally developable light-sensitive layers on a support. A full-color light-sensitive material generally has three thermally developable light-sensitive layers having different color sensitivities, each light-sensitive layer forming or releasing a dye of different color as a result of thermal development. A blue-sensitive layer is usually combined with a yellow dye, a green-sensitive layer with a magenta dye, and a red-sensitive layer with a cyan dye. Other combinations may of course be employed. Combination with a near infrared sensitive layer is also possible.

The choice of layer arrangements depends on the objective of a specific use. For instance, a support is coated with a red-sensitive, a green-sensitive and a blue-sensitive layer, or in the reverse order (i.e., a blue-sensitive, a green-sensitive and a red-sensitive layer), or a support may be coated with a green-sensitive, a red-sensitive and a blue-sensitive layer.

Besides the thermally developable light-sensitive layers described above, the heat-processible color photosensitive material of the present invention may incorporate non-light-sensitive layers such as a subbing layer, an intermediate layer, a protective layer, a filter layer, a backing layer and a release layer. The thermally developable light-sensitive layers and these non-light-sensitive layers may be applied to a support by coating techniques that are similar to those commonly employed to coat and prepare ordinary silver halide light-sensitive materials.

The heat-processible color photosensitive material of the present invention can be produced by forming photographic constituent layers on a support. Usable support include: synthetic plastic films such as a polyethylene film, a cellulose acetate film, a polyethylene terephthalate film, and a polyvinyl chloride film; paper supports such as a photographic raw paper, printing paper, art paper, cast-coated paper, baryta paper and resin-coated paper; and supports prepared by coating these materials with electron-beam curable resin compositions, followed by curing of the same.

The heat-processible color photosensitive material of the present invention is developed after imagewise exposure and this can usually be done merely by heating the material at a temperature in the range of 80 - 200 °C, preferably 100 - 170 °C, for a period of from 1 - 180 seconds, preferably 1.5 - 120 seconds. A diffusible dye may be transferred onto an image-receiving layer simultaneously with thermal development by bringing the image-receiving layer in the image-receiving member into intimate contact with the light-sensitive surface of the light-sensitive material; alternatively, the light-sensitive material brought into intimate contact with the image-receiving member after thermal development may be subsequently heated. In another method, water is supplied before the two members are brought into intimate contact with each other and the assembly is subsequently heated if desired. The light-sensitive material may be preliminarily heated in the temperature range of 70 - 180 °C prior to exposure. In order to enhance the adhesion between the light-sensitive material and the image-receiving member, they may be separately heated at a temperature of 80 - 250 °c just prior to thermal development and transfer, as described in JP-A-60-143338 and JP-A-61-162041.

The heat-processible color photosensitive material of the present invention permits the use of various heating techniques.

All methods of heating that can be used with ordinary heat-processible color photosensitive materials may be applied to the heat-processible color photosensitive material of the present invention. In one instance, the light-sensitive material may be brought into contact with a heated block or plate, or with heated rollers or a hot drum. Alternatively, the material may be passed through a hot atmosphere. High-frequency heating is also applicable. In still another method, an electroconductive layer containing a conductive material such as carbon black is provided either on the back side of the light-sensitive material of the present invention or on the surface of an image-receiving member for heat-transfer and an electric current is applied to generate the Joule heat as heating energy. The heating pattern is in no way limited; preheating may be followed by another cycle of heating; heating may be performed for a short period at high temperatures or for a long period at low temperatures; the temperature may be elevated and lowered continuously; repeated cycles of heating may be employed; the heating may be discontinuous rather than continuous. In any event, a simple heating pattern is preferred. If desired, exposure and heating may proceed simultaneously.

As already mentioned, an image-receiving member is used if the heat-processible color photosensitive material of the present invention is of a transfer type. Any image-receiving member may effectively be used in the present invention if the image-receiving layer employed has a capability for accepting the dye released or formed in the thermally developable light-sensitive layer as a result of thermal development. A preferred example is a polymer containing a tertiary amine or a quaternary ammonium salt, as described in USP 3,709,690. Typical image-receiving layers suitable for use in diffusion transfer can be prepared by coating a support with a mixture in which a polymer containing an ammonium salt or a tertiary amine is combined with gelatin or polyvinyl alcohol. Another useful dye-receiving layer may be formed of a heat-resistant organic high-molecular substance having a glass transition point of 40 - 250 °c as described in JP-A-57-207250.

These polymers may be carried as image-receiving layers on a support; alternatively, they may be used as supports on their own.

Synthetic polymers having glass transition points of 40 °C and above as described in "Polymer Handbook", 2nd ed., edited by J. Brandrup and E. H. Immergut, John Wiley & Sons are also useful polymers. Useful molecular weights of these high-molecular substances are generally in the range of 2,000 - 200,000. These high-molecular substances may be used either independently or as blends. Two or more monomers may be employed to make copolymers.

Particularly preferred image-receiving layers include the polyvinyl chloride layer described in JP-A-59-223425 and the layer described in JP-A-60-19138 that comprises a polycarbonate and a plasticizer.

The polymers described above may be used as supports that also serve as image-receiving layers to form image-receiving members. In this case, the support may be formed of a single layer or two ore more layers.

Supports for image-receiving members may be transparent or non-transparent. Illustrative supports include: films of polymers such as polyethylene terephthalate, polycarbonate, polystyrene, polyvinyl chloride, polyethylene and polypropylene; supports having pigments such as titanium oxide, barium sulfate, calcium carbonate and talc incorporated in these plastic films; baryta paper; resin-coated (RC) paper having paper laminated with pigment-loaded thermoplastic resins; fabrics; glass; metals such as alminum; supports prepared by coating these materials with pigment-loaded electron beam curable resin compositions, followed by curing of the latter; and supports having pigment-loaded coating layers on these materials. Also usable as a support is the cast-coated paper described in JP-A-62-283333.

Particularly useful are the support prepared by coating paper with a pigment-loaded elctron-beam curable resin composition, followed by curing of the resin, and the support prepared by applying a pigment coating layer to paper, which is then coated with an electron-beam curable resin composition, followed by curing of the resin. These supports can immediately be used as image-receiving layers since the resin layer itself serves as an image-receiving layer.

The heat-processible color photosensitive material of the present invention may be of a "monosheet" type that has both a light-sensitive layer and an image-receiving layer formed on the same support, as described in Research Disclosure (RD) No. 15108 and JP-A-57-198458, JP-A-57-207250 and JP-A-61-80148.

The heat-processible color photosensitive material of the present invention and/or the image-receiving member are preferably provided which a protective layer.

The protective layer may contain a variety of additives that are commonly employed in the photographic industry. Suitable additives include matting agents, colloidal silica, slip agents, organofluoro compounds (in particular, fluorine-based surface active agents), antistats, uv absorbers, high-boiling organic solvents, antioxidants, hydroquinone derivatives, polymer latices, surface-active agents (including high-molecular surface-active agents), hardeners (including high-molecular hardeners), particulate organic silver salts, non-light-sensitive silver halide grains, antifoggants, development accelerators, etc.

For details of these additives, reference should be made to Research Disclosure, Vol. 170, No. 17029, June, 1978, and JP-A-62-135825.

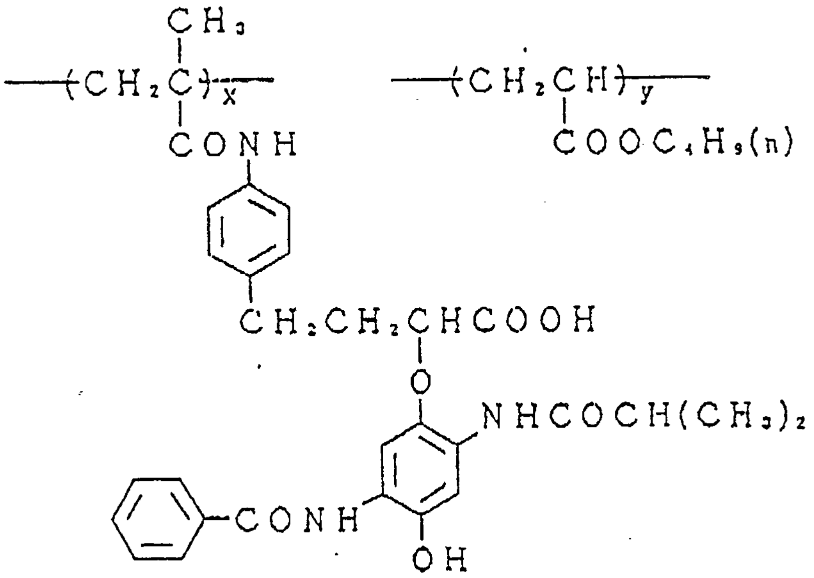
[Working Examples]

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1

A multi-layered photosensitive material (sample No. 1) having the composition shown in Table 1 was prepared. The high-molecular weight dye-providing materials, reducing agent (CDP), thermal solvent (A), restrainer (A) and scavenger (A) that are mentioned in Table 1 had the following structures.

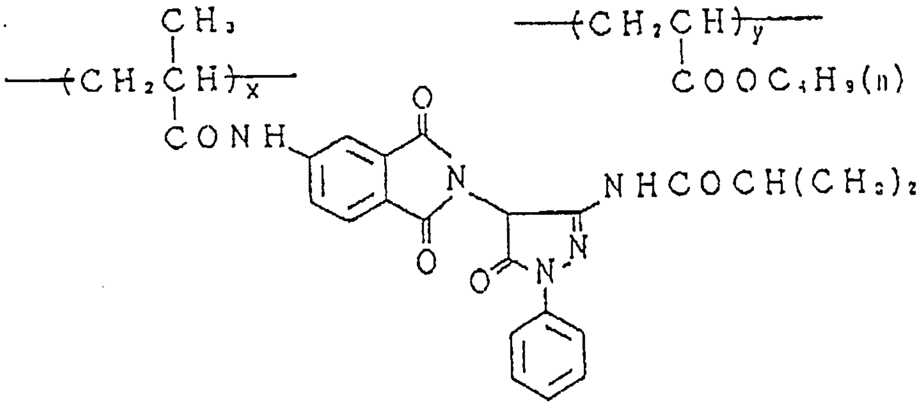
Dye-providing material (1):



x : 45 wt%

y : 55 wt%

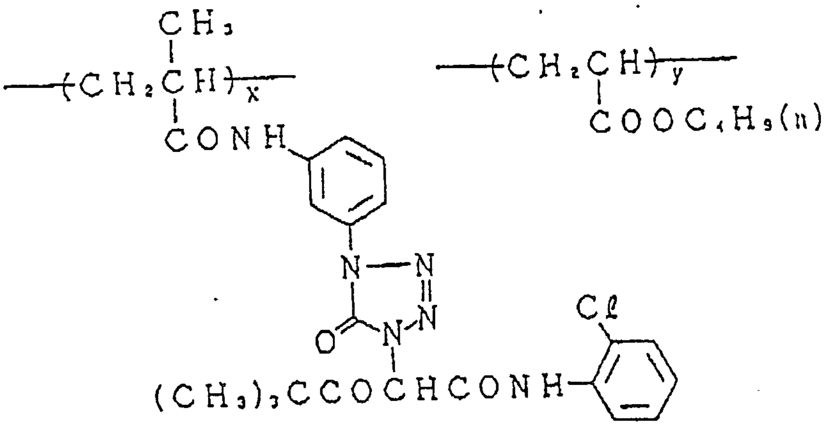
Dye-providing material (2):



x : 40 wt%

y : 60 wt%

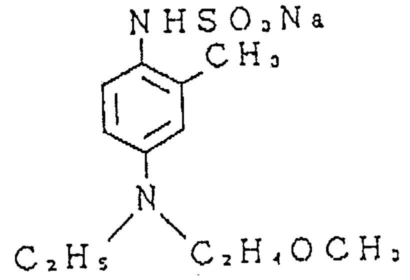
Dye-providing material (3):



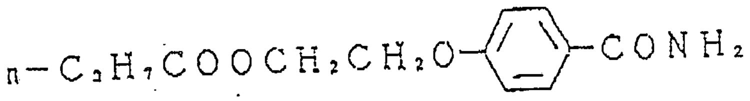
x : 70 wt%

y : 30 wt%

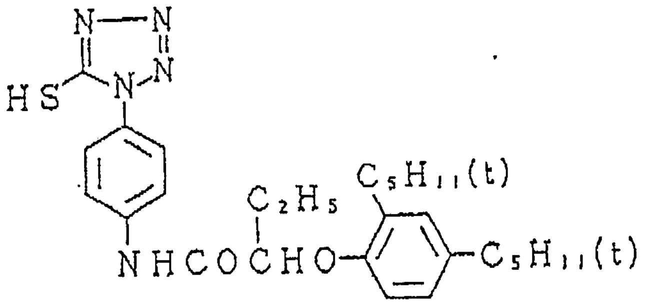
Reducing agent (CDP):



Thermal solvent (A):



Restrainer (A):



Scavenger (A):

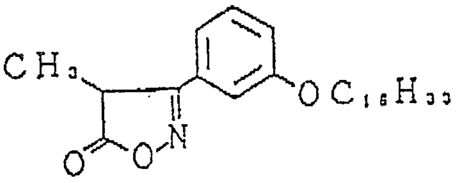


Table 1

Seventh layer	Protective layer	Gelatin, 1.0 g; polyvinylpyrrolidone (K-30), 0.2 g; reducing agent (CDP), 0.34 g, tricresyl phosphate, 0.2 g
Sixth layer	Blue-sensitive layer	Benzotriazole silver, 1.5 g; reducing agent, 1.0 g; tricresyl phosphate, 0.344 g; dye-providing material (1), 1.2 g; blue-sensitive silver halide emulsion, 0.45 g Ag; gelatin, 3.0 g; polyvinylprrolidone (K-30); 0.4 g; thermal solvent (A), 4.0 g; restrainer (A); 0.02 g; scavenger (A), 0.1 g
Fifth layer	Second intermediate layer	Gelatin, 1.55 g; reducing agent, 0.53 g; tricresyl phosphate, 0.22 g; yellow filter dye (F-1), 0.1 g
Fourth layer	Green-sensitive layer	Benzotriazole silver, 0.8 g; reducing agent, 0.675 g; tricresyl phosphate, 0.2 g; dye-providing material (2), 0.9 g; green-sensitive silver halide emulsion, 0.457 g Ag; gelatin, 2.0 g; polyvinylpyrrolidone (K-30), 0.3 g; thermal solvent (A), 3.45 g; restrainer (A), 0.008 g; scavenger (A), 0.08 g

Third layer	First intermediate layer	Gelatin, 1.5 g; reducing agent, 0.49 g; tricresyl phosphate, 0.2 g
Second layer	Red-sensitive layer	Benzotriazole silver, 1.6 g; reducing agent, 1.0 g; tricresyl phosphate, 0.33 g; dye-providing material (3), 1.2 g; red-sensitive silver halide emulsion, 0.68 g Ag; gelatin, 3.0 g; polyvinylpyrrolidone (K-30), 0.6 g; thermal solvent (A), 4.5 g; restrainer (A), 0.016 g; scavenger (A), 0.1 g
First layer	Gelatin layer	Gelatin, 2.5 g
	Support	Latex-subbed transparent polyethylene terephthalate film with a thickness of 180 µm

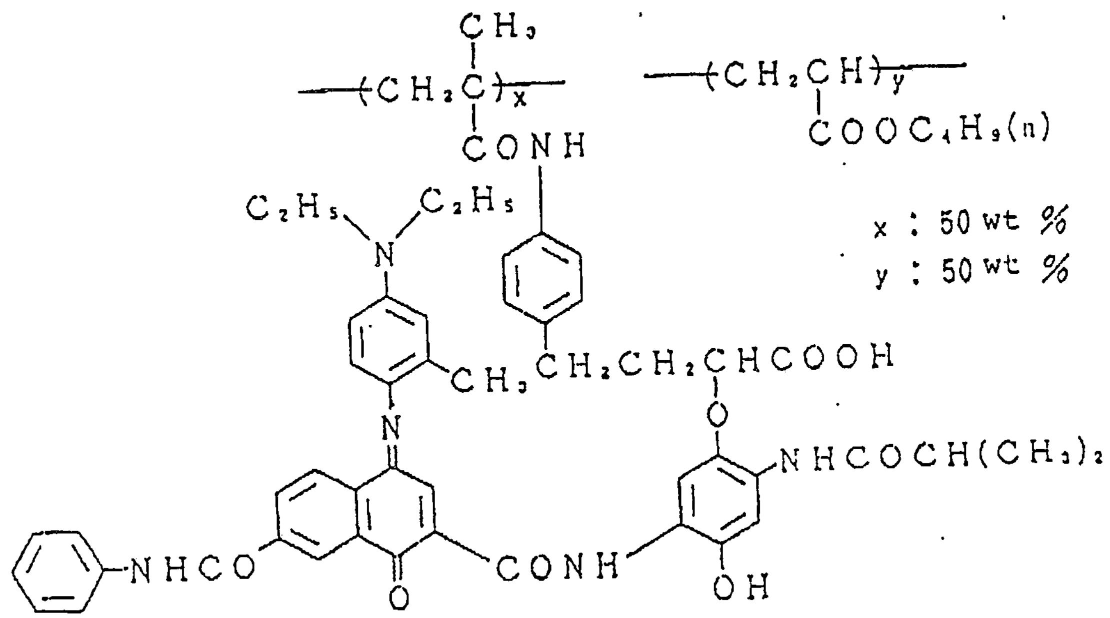
Note: The amount of each addition is indicated in terms of deposit per square meter, provided that the deposits of silver halides are calculated for silver. Each layer additionally contained a surfactant and a hardener in small amounts.

Another photosensitive material (sample No. 2) was prepared by repeating the procedure described above except that the composition of the sixth layer (blue-sensitive layer) was changed as shown below.

Composition of the sixth layer in sample No. 2	
Benzotriazole	2.5 g
Reducing agent (CDP)	1.6 g
Dibutyl phthalate	0.4 g
High-molecular weight dye-providing material (1)	0.8 g
Blue-sensitive silver halide emulsion	076 g Ag
Gelatin	4.8 g
Polyvinylpyrrolidone (K-30)	0.6 g
Thermal solvent (A)	6.0 g
Compound (17) of the present invention	1.0 g
Restrainer (A)	0.025 g
Scavenger (A)	0.16 g

Additional photosensitive materials (sample Nos. 3 and 4) were prepared like sample No. 2 except that compound (17) of the present invention was replaced by compound (25) of the present invention and comparative compound (A) (see below), respectively:

Comparative compound (A):



Each of the photosensitive materials (sample Nos. 1 -4) was exposed to white, blue, green and red light through a step wedge and thermally developed at 145° C for 90 sec in superposition on an image-receiver member No. 1 or 2 having the composition shown below. In response to the exposing light used, a black, a cyan, a magenta or a yellow image of high density and low fog was transferred onto the image-receiving member No. 2.

The black image was subjected to reflection density measurements with infrared light (850 nm) and the maximum density (Dmax) and minimum density (fog, Dmin) were as shown in Table 2.

Image-receiving member No. 1

Photographic baryta paper coated with polyvinyl chloride (n = 1,100; product of Wako Pure Chemical Industries, Ltd.) to give a deposit of 15.0 g/m^2.

Image-receiving member No. 2

Same as image-receiving member No. 1 except that nickel stearate (deposit, 1.3 g/m^2) was incorporated in the polyvinyl chloride layer.

Table 2

		Image-receiving member No. 1	Image-receiving member No. 2
Photosensitive material 1	Dmax	0.00	0.00
	Dmin	0.00	0.00
Photosensitive material 2	Dmax	0.11	1.64
	Dmin	0.07	0.09
Photosensitive material 3	Dmax	0.12	1.58
	Dmin	0.07	0.10
Photosensitive material 4	Dmax	0.10	0.10
	Dmin	0.07	0.07

As Table 2 shows, dye images having absorption in the infrared region could be formed when the photosensitive materials containing compounds of the present invention were used in combination with the image-receiving member containing nickel ions.

The same results were obtained even when the nickel ions in the image-receiving member were replaced by copper or cobalt ions.

Example 2

A multi-layered photosensitive material (sample No. 5) having the composition shown in Table 3 was prepared. Another photosensitive material (sample No. 6) was prepared by repeating the same procedure except that compound (2) of the present invention was replaced by compound (21) of the present invention.

Each of the samples was exposed to green, red and infrared light through a step wedge and wire-bar coated with water on the emulsion-coated side. Thereafter, the samples of photosensitive material were thermally developed at 130 °C for 30 sec in superposition on an image-receiving member No. 3, 4 or 5 having the composition shown below. In response to the exposing light used, a cyan, a magenta and a yellow image was transferred onto the image-receiving members.

The cyan image was subjected to reflection density measurements with infrared light (850 nm) and the maximum density (Dmax) and minimum density (fog, Dmin) were as shown in Table 4.

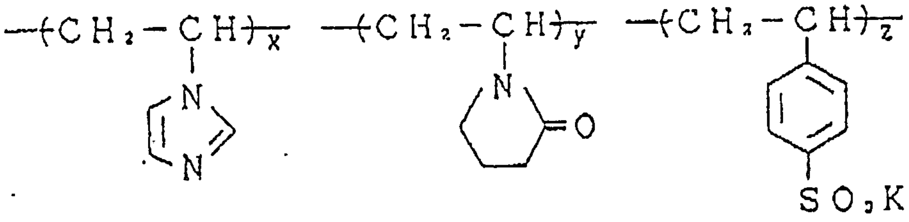
Image-receiving member No. 3

Photographic baryta paper coated with a lime-processed gelatin layer (deposit, 2.3 g/m^2), which in turn was coated with a dye adherent layer having the composition shown below:

Composition of dye adherent layer:

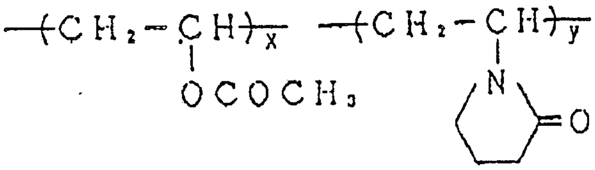
Polymer (I) (see below)	4.25 g/m^2
Polymer (II) (see below)	1.4 g/m^2
Lime-processed gelatin	3 g/m^2

Polymer (I):



x: 60 wt% y: 30 wt% z: 10 wt%

Polymer (II):



x: 30 wt%

y: 70 wt%

Image-receiving member No. 4

Same as image-receiving member No. 3 except that nickel acetate (deposit, 0.6 g/m^2) was incorporated in the dye adherent layer.

Image-receiving member No. 5

Same as image-receiving member No. 3 except that copper acetate (deposit, 0.6 g/m^2) was incorporated in the dye adherent layer.

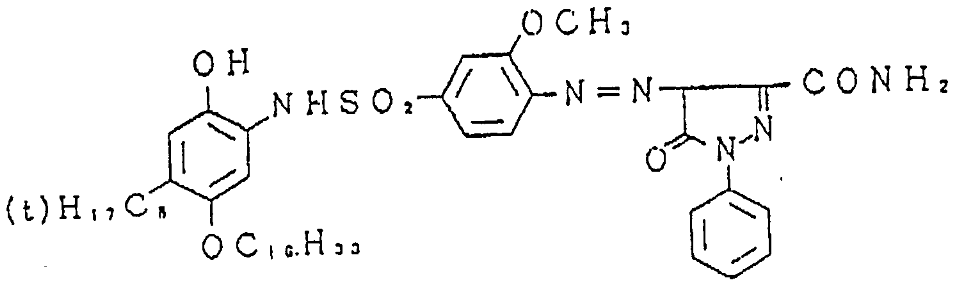
Table 3

Sixth layer	Protective layer	Gelatin, 1 g; guanidinotrichloroacetic acid, 0.33 g;silica (0.4 µm), 0.1 g
Fifth layer	Green-sensitive emulsion layer	Benzotriazole silver, 0.2 g; thermal solvent (B)*1), 0.2 g; green-sensitive silver halide, 0.4 g Ag; dye-providing material (4)*2), 0.4 g; tricresyl phosphate, 0.8 g; gelatin, 1 g; guanidinotrichloroacetic acid, 0.33 g; restrainer (B)*3), 0.01 g
Fourth layer	Intermediate layer	Gelatin, 1.2 g; guanidinotrichloroacetic acid, 0.4 g

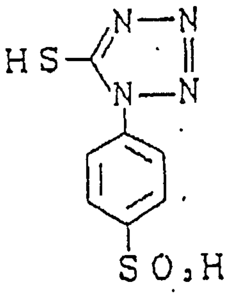
Third layer	Red-sensitive emulsion layer	Benzotriazole silver, 0.2 g; thermal solvent (B)*1), 0.2 g; red-sensitive silver halide, 0.3 g Ag; dye-providing material (5)*4), 0.4 g; guanidinotrichloroacetic acid, 0.33 g; gelatin, 1 g; tricresyl phosphate, 0.6 g; restrainer (B)*3), 0.01 g
Second layer	Intermediate layer	Gelatin, 1.0 g; guanidinotrichloroacetic acid, 0.33 g
First layer	Infrared-sensitive emulsion layer	Benzotriazole silver, 0.3 g; thermal solvent (B)*1), 0.3 g; infrared-sensitive silver halide*5), 0.45 g Ag; dye-providing material (6)*6), 0.3 g; compound (2) of the present invention, 0.2 g; guanidinotrichloroacetic acid, 0.5 g; gelatin, 1.5 g; tricresyl phosphate, 0.8 g; restrainer (B)*3), 0.015 g
	Support	Latex-subbed transparent polyethylene terephthalate film having a thickness of 180 µm

*1) Thermal solvent (B): benzenesulfonamide

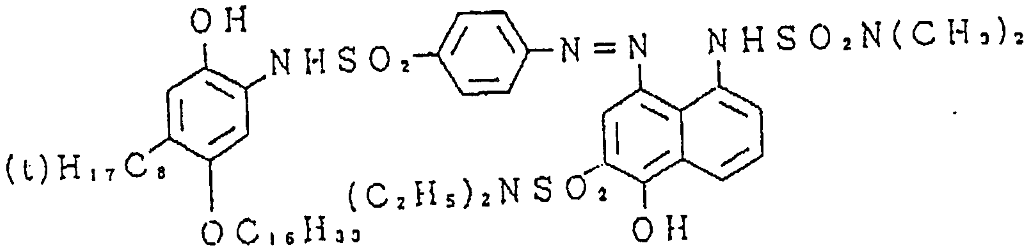
*2) Dye-providing material (4):



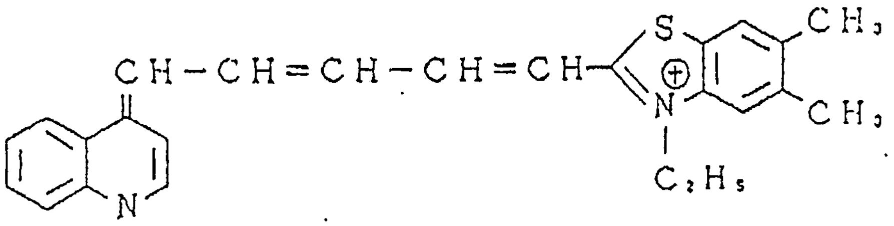
*3) Restrainer (B):



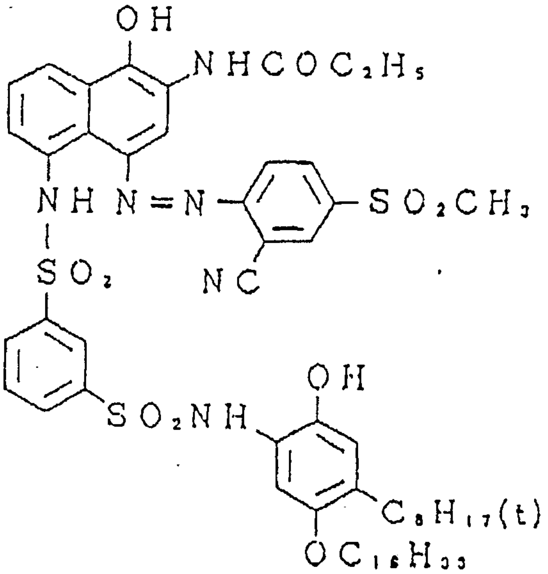
*4) Dye-providing material (5):



*5) Spectrally sensitized with the following:



*6) Dye-providing material (6):



The images obtained on the image-receiving member (Nos. 3, 4 and 5) were exposed for 24 h under a xenon lamp (6,000 W) to give a light intensity of 60,000 lux on the surface of each image-receiving layer. Maximum density was measured both before and after the exposure (Do before exposure and D after exposure) and the percentage of residual image [{D/Do) × 100 (%)] was calculated to evaluate the lightfastness of each image. The images were also left in a hot and humid atmosphere (60 °C × 70% r.h.) for 7 days and their heat resistance was evaluated by calculating the percentage of residual image from the maximum density as measured both before and after the storage. Values higher than 90% would be acceptable for practical purposes with respect to both lightfastness and heat resistance.

Table 4

Photosensitive material	Image-receiving member	Dmax	D min, %	Lightfastness, %	Heat resistance
5	3	0.03	0.02	-	-
	4	1.46	0.31	94	96
	5	1.53	0.32	96	97
6	3	0.04	0.02	-	-
	4	1.35	0.33	93	94
	5	1.40	0.34	92	95

As Table 4 shows, dye images having absorption in the infrared region could be obtained when photosensitive materials using compounds of the present invention were employed in combination with image-receiving members incorporating metallic ions. The lightfastness and heat resistance of the images obtained were high enough to meet practical needs.

An additional photosensitive material was prepared by repeating the procedure for the preparation of sample No. 5 except that nickel stearate (deposit, 1.0 g/m^2) was incorporated in the protective layer. With this photosensitive material, a satisfactory image was formed of the infrared dye even when it was used in combination with the image-receiving member No. 3. The Dmax of this image was 1.12.

Example 3

A multi-layered photosensitive material (sample No. 7) having the composition shown in Table 5 was prepared. Another photosensitive material (sample No. 8) was prepared by repeating the same procedure except that compound (17) of the present invention was replaced by compound (24) of the present invention.

Table 5

Sixth layer	Protective layer	Gelatin, 1.0 g; polyvinylpyrrolidone (K-30), 0.2 g; reducing agent (CDP), 0.34 g; tricresyl phosphate, 0.2 g
Fifth layer	Green-sensitive layer	Benzotriazole silver, 1.5 g; green-sensitive silver halide, 0.45 g Ag; reducing agent, 1.0 g; dye-providing material (3), 0.8 g: gelatin, 3.0 g; polyvinylpyrrolidone (K-30), 0.4 g; thermal solvent (A), 4.0 g; tricresyl phosphate, 0.4 g; restrainer (A), 0.02 g; scavenger (A), 0.1 g
Fourth layer	Intermediate layer	Gelatin, 1.55 g; reducing agent, 0.5 g; tricresyl phosphate, 0.2 g
Third layer	Red-sensitive layer	Benzotriazole silver, 0.8 g; red-sensitive silver halide, 0.46 g Ag; reducing agent, 0.68 g; dye-providing material (2), 0.9 g; gelatin, 2.0 g; polyvinylpyrrolidone (K-30), 0.3 g; thermal solvent (A), 3.45 g; tricresyl phosphate, 0.2 g; restrainer (A), 0.02 g; scavenger (A), 0.1 g

Second layer	Intermediate layer	Gelatin, 1.5 g; reducing agent, 0.5 g; tricresyl phosphate, 0.2 g
First layer	Infrared-sensitive layer	Benzotriazole silver, 2.4 g; infrared-sensitive silver halide*7), 1.0 g Ag; reducing agent, 1.5 g; dye-providing material (1), 1.5 g; gelatin, 4.5 g; polyvinylpyrrolidone (K-30), 0.9 g; thermal solvent (A), 6.7 g; restrainer (A), 0.024 g; scavenger (A), 0.15 g; compound (17) of the present invention, 0.8 g; tricresyl phosphate, 1.0 g

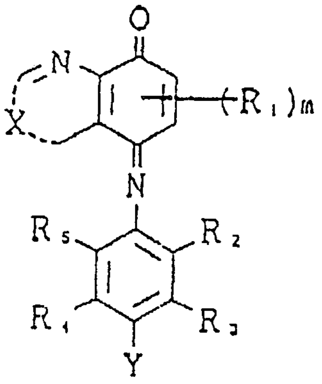
*7) Spectrally sensitized with the same sensitizer as in Example 2.

Each of the photosensitive materials (sample Nos. 7 and 8) was exposed as in Example 2 and subsequently processed as in Example 1 in superposition on the image-receiving member No. 2. In response to the exposing light, a cyan, a magenta and a yellow image of high density and low fog were transferred onto the image-receiving member No. 2. Further, an image was also formed of the infrared dye in the cyan image forming area.

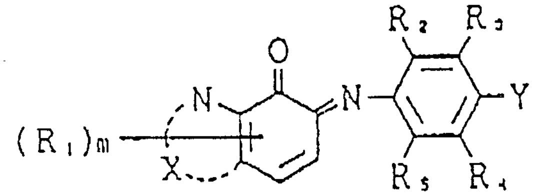
As will be understood from the foregoing description, the present invention is capable of producing an infrared dye image that is highly stable under exposure to heat and light and that has an absorption wavelength that allows for reading with infrared radiation.

Claims

1. An image forming method which comprises the steps of: providing a heat-processible color photosensitive material that has at least a light-sensitive silver halide, a reducing agent, a binder and a dye-providing material on a support, which dye-providing material contains either a dye portion represented by the following general formula (1) or a dye portion represented by the following general formula (2) or both; performing imagewise exposure on said photosensitive material; subsequent to or simultaneously with the imagewise exposure, thermally developing said photosensitive material in close contact with an image-receiving material; transferring onto said image-receiving material all or part of the diffusible dye containing said dye portion which is formed from said dye-providing material as a function of development; during or after the transfer, chelating part or all of the diffusible dye with a metal to thereby form an image of the chelated dye in said image-receiving material:

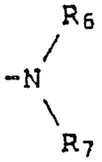


(1)



(2)

where X represent the atomic group necessary to form an aromatic nitrogenous heterocyclic ring; R_1 is a hydrogen atom, a halogen atom or a monovalent organic group; m is an integer of 0 or 1 - 3, provided that when m is 2 or 3, R_1 may be the same
or different; Y is a hydroxyl group or a group



$$-N\begin{matrix} R_6 \\ R_7 \end{matrix}$$

(where R and R_7 each represents a hydrogen atom or an optionally substituted alkyl group); and R^2, R^3, R^4 and R^5 each represents a hydrogen atom, a halogen atom, or a monovalent organic group.

2. A method according to claim 1 wherein the dye portion represented by the general formula (1) or (2) forms a chelate either within the image-receiving layer of said image-receiving member or in a nearby area.

3. A method according to claim 1 wherein X in the general formula (1) or (2) is an atomic group capable of forming a condensed pyridine ring.

4. A method according to claim 1 wherein the monovalent organic group represented by R_1 is an alkyl group, an alkoxy group, , $-CONR_6R_7$, $-NHCOR_8$, $-NHCO_2R_8$, $-NHSO_2R_8$, $-NHSO_2NR_6R_7$, $COOR_8$, $-SO_2R_8$, $-NHCOR_6R_7$ or a cyano group, wherein R^6 and R^7 each represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group, and R_8 represents a hydrogen atom, an alkyl group, an aryl group, a cycloalkyl group, a heterocyclic group or an amino group.

5. A method according to claim 4 wherein each of R_6 and R_7 is an alkyl group having 1 - 4 carbon atoms.

6. A method according to claim 1 wherein R_1 in the general formula (1) represents a halogen atom or a monovalent organic group and is in the position ortho to the group $>C = 0$.

7. A method according to claim 1 wherein R_1 in the general formula (2) represents a halogen atom or a monovalent organic group and is in the position para to the group $>C = 0$.

8. A method according to claim 1 wherein a compound capable of supplying metallic ions for the formation of the metal chelate is an organic or inorganic salt of metallic ions or a complex thereof.

9. A method according to claim 8 wherein said metallic ions are those of a divalent transition metal.

10. A method according to claim 9 wherein said divalent transition metal is selected from among nickel,

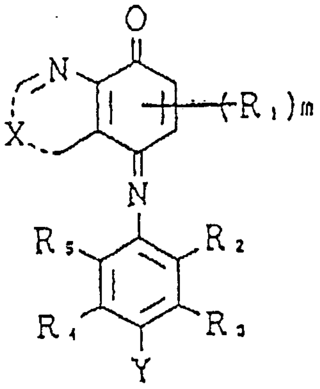
copper, zinc, cobalt, platinum and palladium.

11. A method according to claim 8 wherein said compound capable of supplying metallic ions in incorporated in the photosensitive material in an amount of 0.1 - 10 moles per mole of said dye-providing material.

12. A method according to claim 1 wherein said dye-providing material is used in an amount of 0.005 to 50 g per square meter of the photosensitive material.

13. A method according to claim 1 wherein said dye-providing material is used in an amount of 0.1 to 10 g per square meter of the photosensitive material.

14. A heat-processible color photosensitive material that has at least a light-sensitive silver halide, a reducing agent, a binder and a dye-providing material on a support wherein said dye-providing material contains either a dye portion represented by the following general formula (1) or a dye portion represented by the following general formula (2) or both:



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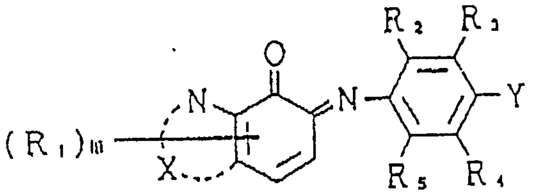
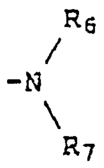


(2)·

where X represent the atomic group necessary to form an aromatic nitrogenous heterocyclic ring; R_1 is a halogen atom or a monovalent organic group; m is an integer or 0 or 1 - 3, provided that when m is 2 or 3, R_1 may be the same or different; Y is a hydroxyl group or a group



$$-N\begin{matrix} R_6 \\ R_7 \end{matrix}$$

(where R and R_7 each represents a hydrogen atom or an optionally substituted alkyl group); and R^2, R^3, R^4 and R^5 each represents a hydrogen atom, a halogen atom, or a monovalent organic group.