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(54) A heat developing color photosensitive material.

(57) A heat developing color photosensitive material is disclosed. The material comprises a support having thereon a photosensitive silver halide, a reducing agent and a dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region from 400 nm to 700 nm, wherein said support further has thereon an infrared dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region longer than 725 nm.

A HEAT DEVELOPING COLOR PHOTOSENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a heat developing color photosensitive material, in particular, to a similar material capable of providing a color image by heat developing, and is also capable of providing recorded information that can be read with light of a longer wavelength region than 750 nm.

BACKGROUND OF THE INVENTION

Recently, a part of development effort for an information recording medium such as an ID card is centered on a technique for simultaneously storing character data or signal data such as bar codes, as well as color image data, in such a recording medium. Such a recording medium storing character data, signal data and the like is often subjected to mechanical reading with light, whose wavelength being in a longer wavelength region than 750 nm, emitted from a semiconductor laser or LED, in order to expedite data processing and prevent erroneous data reading.

Meanwhile, the silver halide color photosensitive material is a most excellent medium in terms of quality of color image. Therefore, there is a development effort on an information recording medium based on a silver halide color photosensitive material. However, since a conventional silver halide color photosensitive material is treated by a wet process, there remain many problems in terms of simplicity and rapidness in photographic process.

A heat developing color photosensitive material, in particular, a diffusion transfer heat developing color photosensitive material is known as a material that is capable of providing good image quality of a silver halide color photosensitive material and allows simplicity and rapidness in photographic process.

This diffusion transfer heat developing color photosensitive material and image formation with such a material is disclosed, for example, in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) Nos. 12431/1984, 159159/1984, 181345/1984, 229556/1984, 2950/1985, 52643/1986, 61158/1986, 61157/1986, 180550/1984, 132952/1986 and 139842/1986, and U.S. Patent Nos. 4,595,652, 4,590,154 and 4,584,267.

Since such a diffusion transfer heat developing color photosensitive material usually incorporates a dye providing substance that forms or releases dyes of three colors, i.e. yellow, magenta and cyan, it is difficult to read out prestored information by using light whose wavelength being in a longer wavelength region than 750 nm.

A photographic material comprising an infrared dye capable of being read out character data and/or signal data using light of the wavelength longer than 750nm is known, i.e.,sound truck. Therefore, a recording material capable of being read out character data and/or signal data using light of the wavelength longer than 750nm can be obtained by various kinds of a photographic process.

However, in an instant photographic process, an infrared dye is readily decomposed in high alkali treatment and an image having high reflectance density at the wavelength longer than 750nm can not be obtained. And, also, on account of low resolving power, a record highly accumulated can not be obtained.

In a heat sensitive transfer process, an infrared dye is readily decomposed in high temperature treatment and an image having high reflectance density at the wavelength longer than 750nm can not be obtained.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a heat developing color photosensitive material that is capable of providing a high quality color image or character data or signal data and is capable of being treated with a simple and rapid photographic process.

Another object of the invention is to provide a heat developing color photosensitive material that is capable of recording character data and signal data and the like that are read out using light whose wavelength is longer than 750 nm, in conjunction with color image.

Further another object of the invention is to provide a heat developing color photosensitive material capable of recording character data and/or signal data which have high reflectance density at the wavelength longer than 750nm, together with color image.

DETAILED DESCRIPTION OF THE INVENTION

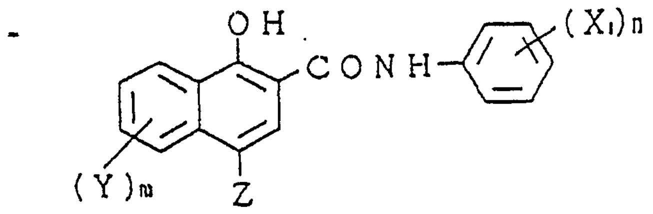
The inventors, as a result from devoted studies for solving the above-mentioned objects, have learned that these objects of the invention are attained by a heat developing color photosensitive material comprising a support having thereon photosensitive silver halide, a reducing agent, and a dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region from 400 nm to 700 nm, wherein said support further has thereon an infrared dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region longer than 725 nm.

The present invention is hereunder described in detail.

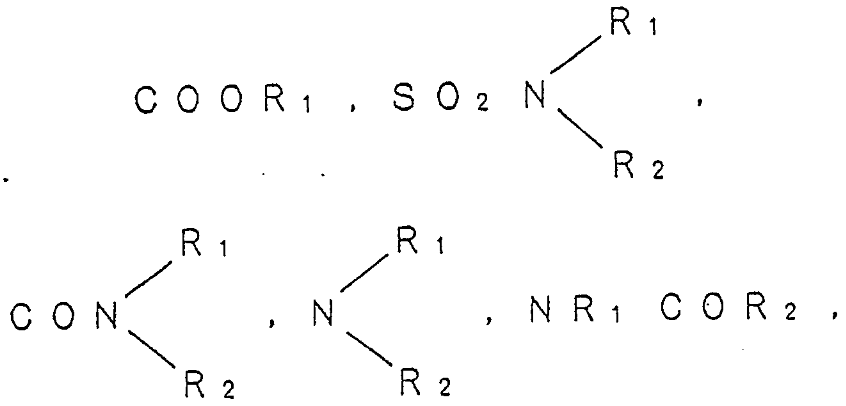
First, description is centered on a compound capable of releasing or forming a dye whose absorption maximum is in a longer wavelength region than 725 nm (hereinafter called an IR dye), and, incidentally, this type of compound is hereinafter called an IR dye providing substance. An IR dye providing substance is a compound capable of releasing or forming an IR dye in correspondence with or in reversely correspondence with the developing of silver, and examples of a useful such compound include reduction dye-releasing compounds described in J.S. Patent Nos. 4,463,079 and 4,439,513; compounds derived from coupling dye-releasing compounds whose dyes are IR dyes, as described in U.S. Patent No. 4,474,867 and Japanese Patent O.P.I. Publication No. 12431/1984. Among these examples, those particularly preferable are coupling dye-forming compounds.

A preferred coupling dye-forming compound capable of forming an IR dye (hereinafter called an IR coupler) is a naphthol coupler represented by Formula (1) or (2) below:

Formula (1)



wherein X_1 represents an electron attracting group such as a halogen atom (e.g. chlorine, bromine, and fluorine), a cyano group, a carboxylic acid ester group, a carboxylic acid amide group, and sulphonic acid amide; n represents an integer of 1 to 3; when n is 2 or 3, two or three X_1s may be identical to or different from each other;
Y represents

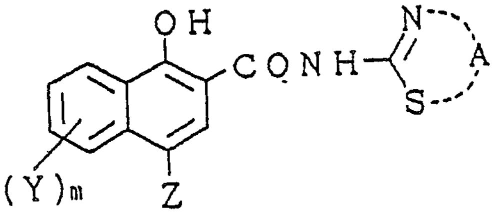


$$COOR_1,\ SO_2N\begin{matrix}R_1\\R_2\end{matrix},\ CON\begin{matrix}R_1\\R_2\end{matrix},\ N\begin{matrix}R_1\\R_2\end{matrix},\ NR_1COR_2,$$

NR_1COR_2, $NR_1SO_2R_2$ or a halogen atom (wherein R_1 and R_2 independently represent a hydrogen atom, an

alkyl group, or an aryl group);
m represents an integer of 0 to 4; when m is not less than 2, a plurality of Y may be identical to or different from each other;
Z represents a hydrogen atom or a group capable of being released by coupling reaction.

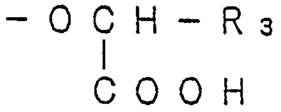
Formula (2)



Y, Z and m are identical with those in Formula (1); A represents a group of atoms (preferably, carbon atoms or nitrogen atoms) needed for forming a 5-membered ring (may have a substituent on the ring), the ring may be condensed with another ring (e.g. a benzene ring). An IR coupler of Formula (1) or (2) preferably has a molecular weight (molecular weight of the other portion than Z) of 700 or less, in particular, 500 or less, in order to improve transferability of an IR dye formed.

In order to enhance immobility in a photosensitive layer and improve solubility to a coupler solvent, an IR coupler of Formula (1) or (2) has a ballast group (preferably an organic group having 8 or more carbon atoms, or a polymer residue), wherein the ballast group preferably has Z as a substituent.

Z represents a hydrogen atom or a group capable of being split off by coupling reaction. Z in Formula (1) or (2) is preferably such a coupling-off group, and the examples of the coupling-off group include a halogen atom (e.g. chlorine, bromine, and iodine), a sulfo group, an alkoxy group, an aryloxy group, a thiocyano group, an acyloxy group, an arylthio group, and a nitrogen heterocycle residue group. Those preferred are groups represented by Formula (3) below.



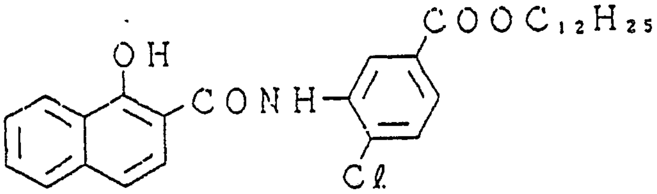
$$-\mathrm{O}\underset{\displaystyle\mathrm{COOH}}{\underset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{R}_3$$

R_3 represents an alkyl group, an alkenyl group, an aralkyl group, an aryl group, each possibly having a substituent group; and a hydrogen atom.

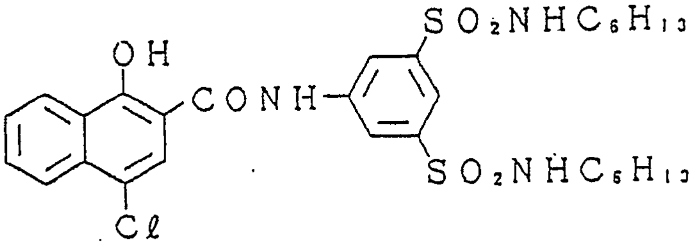
The useful IR coupler can be a copolymer of a coupler represented by Formula (2) and a monomer such as (meth)acrylate or styrene.

The typical examples of the IR coupler are as follows:

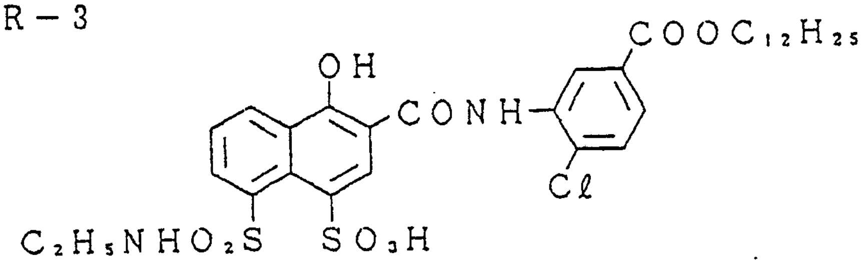
IR−1



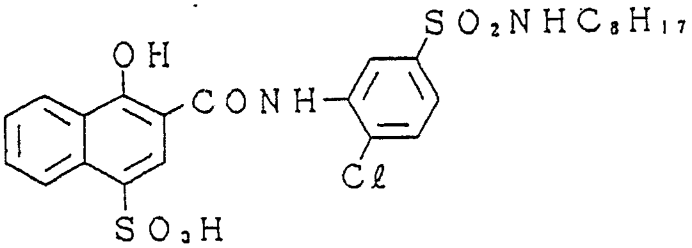
IR−2



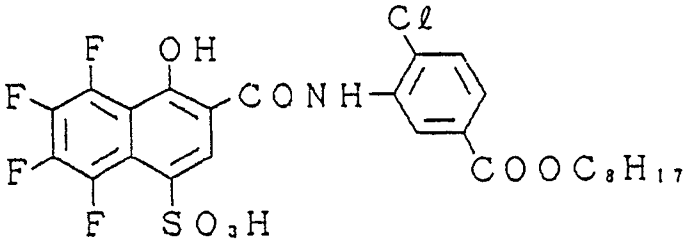
IR−3



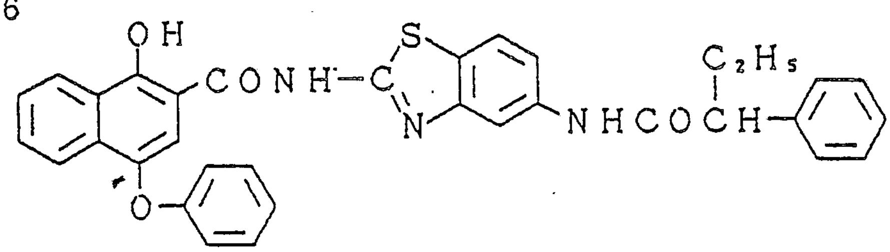
IR−4



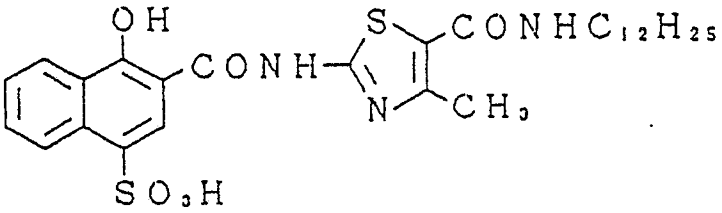
IR−5



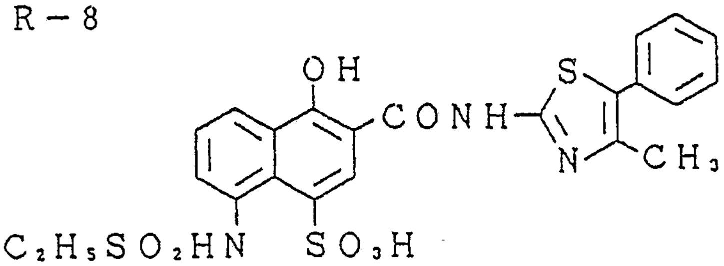
IR-6



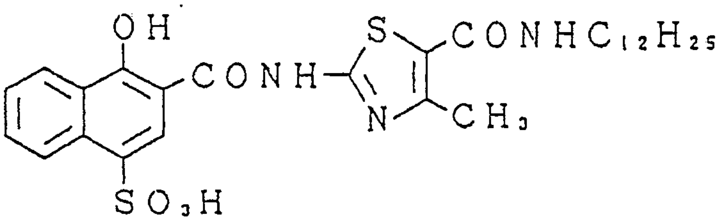
IR-7



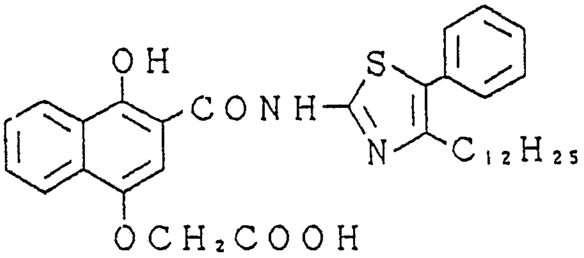
IR-8



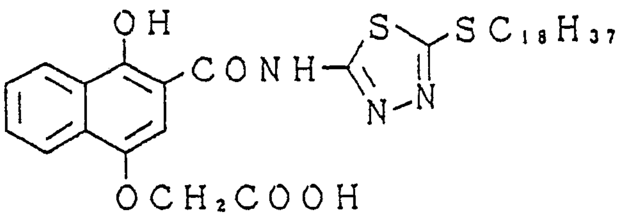
IR-9



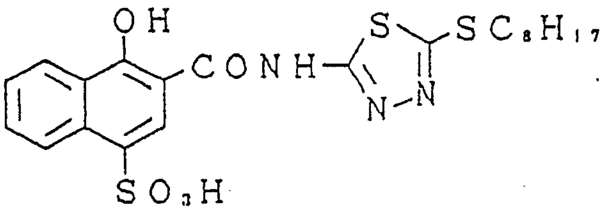
IR-10



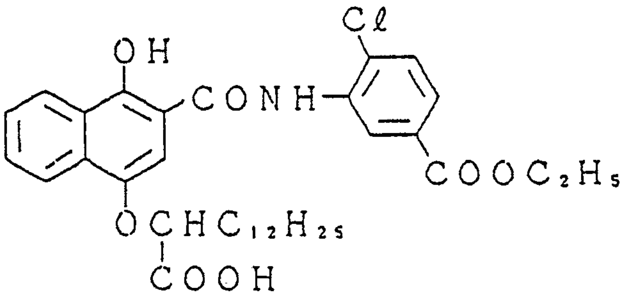
IR-11



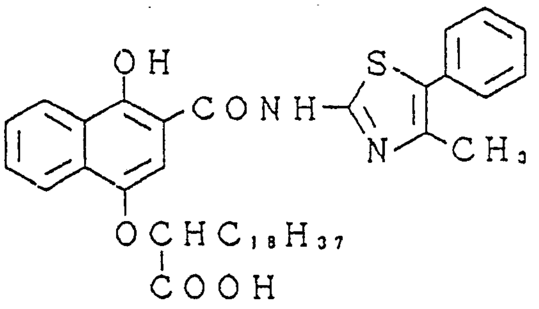
IR-12



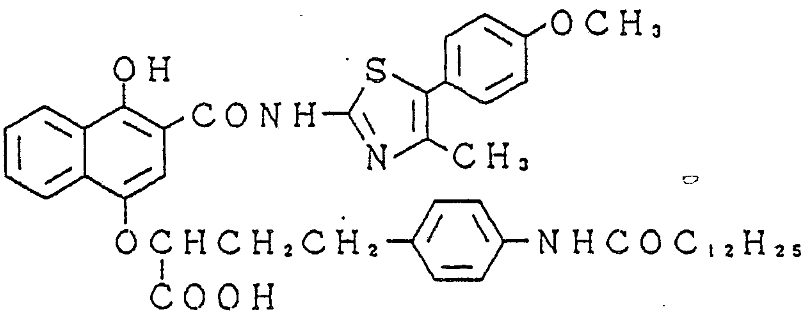
IR-13



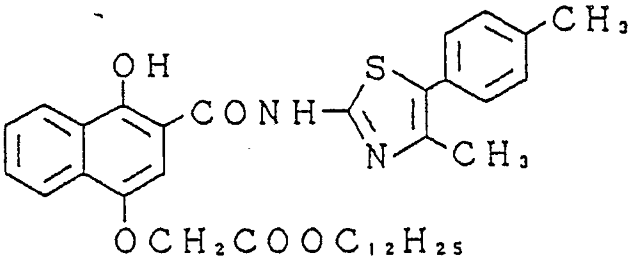
IR-14



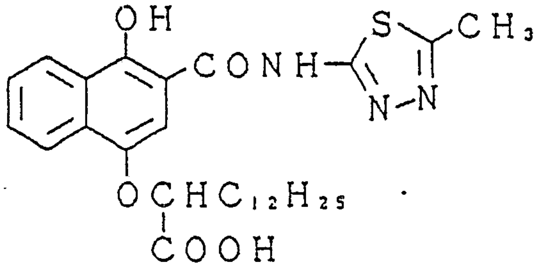
I R−15



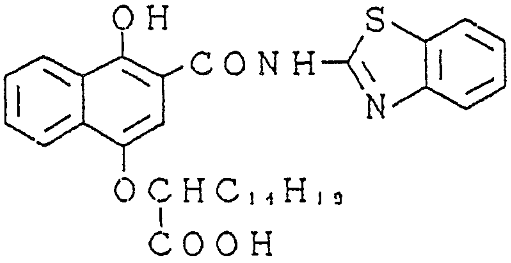
I R−16



I R−17

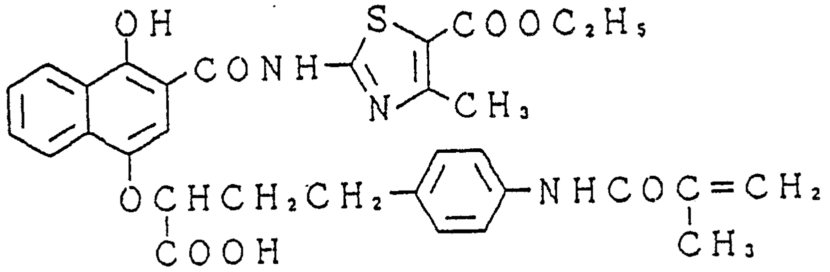


I R−18



IR-19

Copolymer of

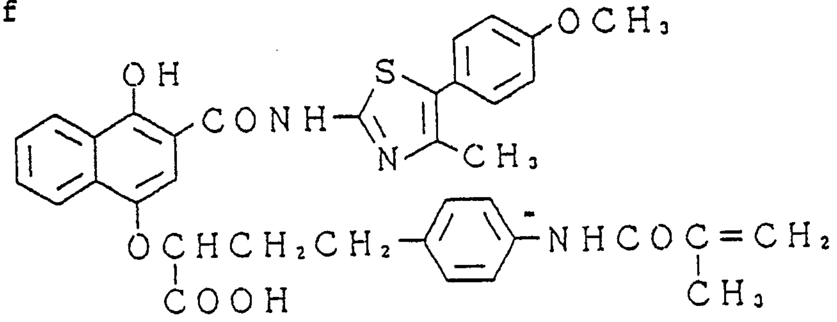


and BA

(Composition ratio: weight ratio = 6:4) BA: butylacrylate

IR-20

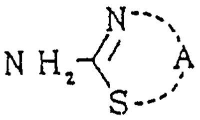
Copolymer of



and BA

(Composition ratio: weight ratio = 5:5)

An IR coupler of Formula (1) or (2) is synthesized by condensing a 1-hydroxy-2-naphthoic acid phenyl ester with a relevant amine {an aniline derivative or



(A is synonymous with that defined for Formula (2)}.

According to the invention, those useful as an IR dye providing substance include a compound represented by Formula (A) below.

Formula (A)

$(Y-L)_{q}X$

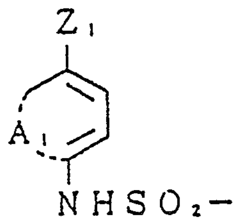
In this formula, X represents an IR dye residue whose λ max is in the wavelength region longer than 725 nm; Y represents a group that has a property which, as a mathematic function of development, varies the diffusibility of post-developing X from that of pre-developing X (this group is known as a "carrier"); L represents a simple link or a bivalent bonding group; q represents 1 or 2.

The carrier is hereunder described.

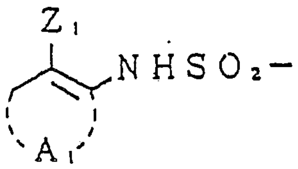
The carrier is categorized into two types, that is a negative type that endows a dye with diffusibility in correspondence (positive function) with developing of silver, and a positive type that endows a dye with diffusibility reversely in correspondence with developing of silver.

Among negative type carriers, there is a reduction type carrier that releases a diffusible dye when oxidized. The examples of this particular carrier are those represented by Formulas (4) through (8) below:

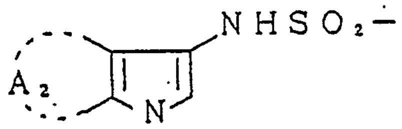
Formula (4)



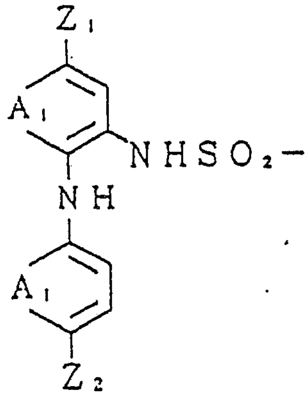
Formula (5)



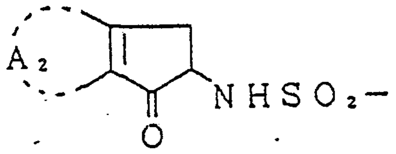
Formula (6)



Formula (7))



Formula (8)



In these formulas (4) through (8), A_1 represents an atomic group needed for forming a benzene ring or naphthalene ring; A_2 represents an atomic group needed for forming a condensed benzene ring.

A ring represented by A_1 or A_2 may have a substituent, and at least one substituent is a ballast group.

Z_1 and Z_2 independently represent a hydroxy group, an amino group (including a substituted amino group) or a group that is capable of providing a hydroxy group or amino group (including a substituted amino group) by hydrolysis.

The typical examples of the above-mentioned carrier are described in Japanese Patent O.P.I. Publication Nos. 33826/1973, 113624/1976, 179840/1982, 116537/1983, 60434/1984, 65839/1984, 165055/1984, 104343/1976 and 124329/1984.

When using, as a dye proving substance of the invention, a compound containing the above-mentioned carrier, the dye providing substance may also function as a reducing agent.

Another negative type carrier is a coupler residue group. The dye portion has a substituent group at an active site of a coupler, and a coupler residue group has at least one ballast group as a substituent group. The typical examples of such a carrier are described in Japanese Patent O.P.I. Publication Nos. 122596/1982, 186744/1982, 159159/1984, 174834/1984, and 231540/1984.

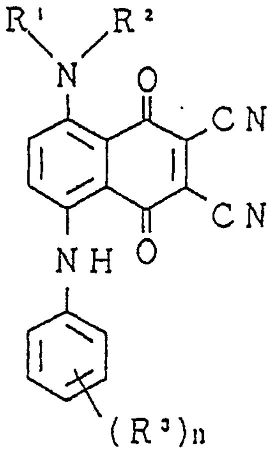
Still another negative type carrier is a coupler having a ballast group as a substituent group at an active site of the coupler, wherein the dye portion has a substituent group other than that at the active site. The typical examples of such a negative type carrier are described in Japanese Patent Application No. 257998/1988.

The typical examples of a positive type carrier are described in Japanese Patent O.P.I. Publication Nos. 63618/1976, 69033/1978, 130927/1979, 111628/1974, 4819/1977, 35533/1978, 110827/1978, 130927/1979 and 164342/1981, and U.S. Patent No. 4,783,396.

The IR dye residue group represented by X is hereunder described.

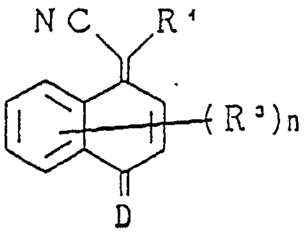
The useful IR dye residue group represent by X is any group as far as its λ max is in 725 to 1000 nm, and, the preferred examples of which are residues of dyes represented by Formulas (9) through (12) below.

Formula (9)



wherein R^1 and R^2 independently represent a possibly substituted alkyl group (e.g. a methyl group, an ethyl group and a methoxyethyl group) having 1 to 4 carbon atoms, or a hydrogen atom; R^3 represents a halogen atom, an alkyl group, an alkoxy group, an alkylamino group, an aralkyl group, a cycloalkyl group, an aryloxy group, an amino group, a sulfonylamino group, an acylamino group, an acyl group, a sulfonyl group, a carbamoyl group, a sulfamoyl group, a ureido group, an alkylthio group, an arylthio group, a hydroxy group, a cyano group or a carboxyl group, each group may have a substituent group; n represents an integer of 0 to 3.

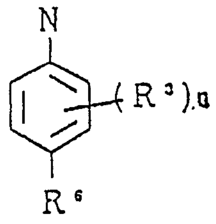
Formula (10)



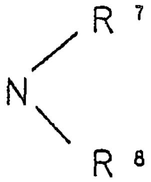
wherein R^4 represents a substituent electron attracting group (particularly preferably, a cyano group or $CONHR^5$, where R^5 is a hydrogen atom, an alkyl or aryl group possibly having a substituent group); R^3 and n are synonymous with those defined for Formula (9).

D is represented by the following Formula E.

Formula E

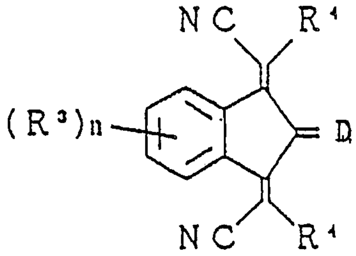


(wherein R^3 and n are synonymous with those defined for Formula (9); R^6 represents a hydroxy group or



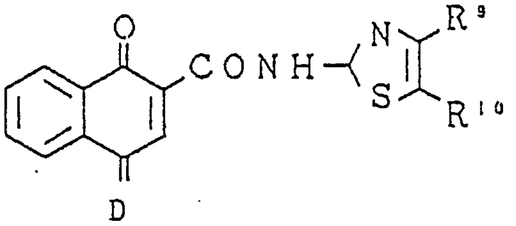
where R^7 and R^8 independently represent a possibly substituted alkyl group); R^7 and R^8, or R^7 and R^3, or R^8 and R^3, may be bonded together to form a ring.)

Formula (11)



wherein R^3, R^4, D and n are synonymous with those defined for Formulas (9) and (10).

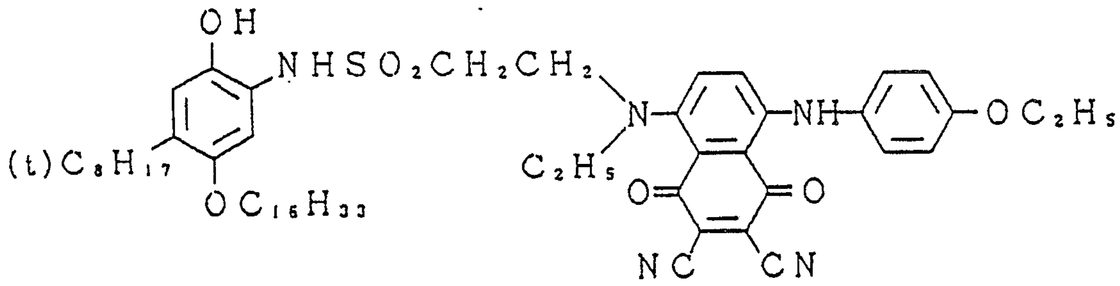
Formula (12)



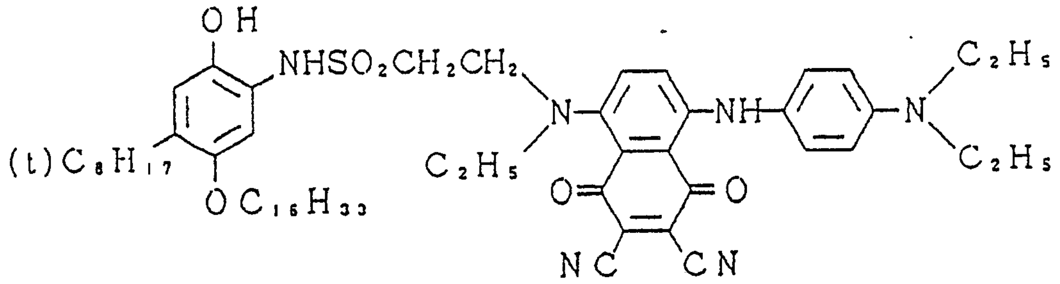
In this formula, D is synonymous with that defined for Formula (10), while R^9 and R^{10} independently represent an alkyl group, an aralkyl group, an aryl group, an alkyloxy group, aryloxy or a hydrogen atom. R^9 and R^{10} may be bonded together to form a ring (e.g. a benzene ring), where each group may have a substituent group.

The typical examples of a compound represented by Formula (A) are as follows.

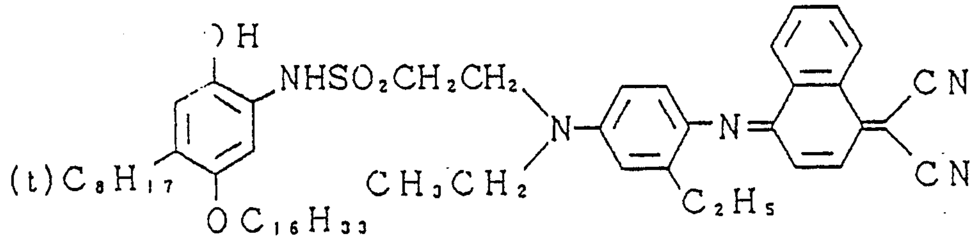
A − 1



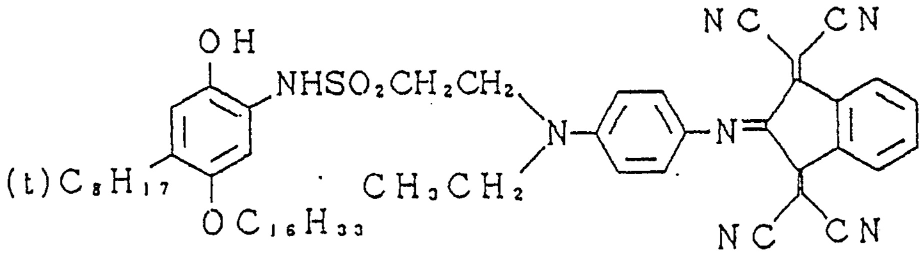
A − 2



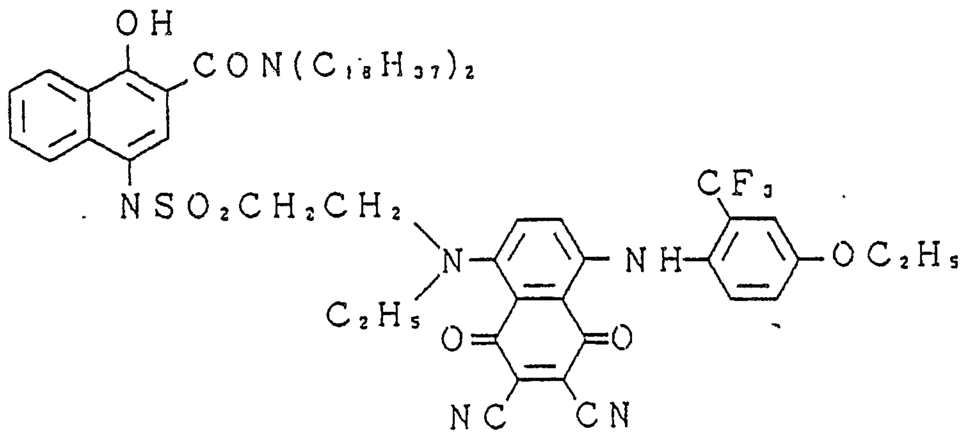
A − 3



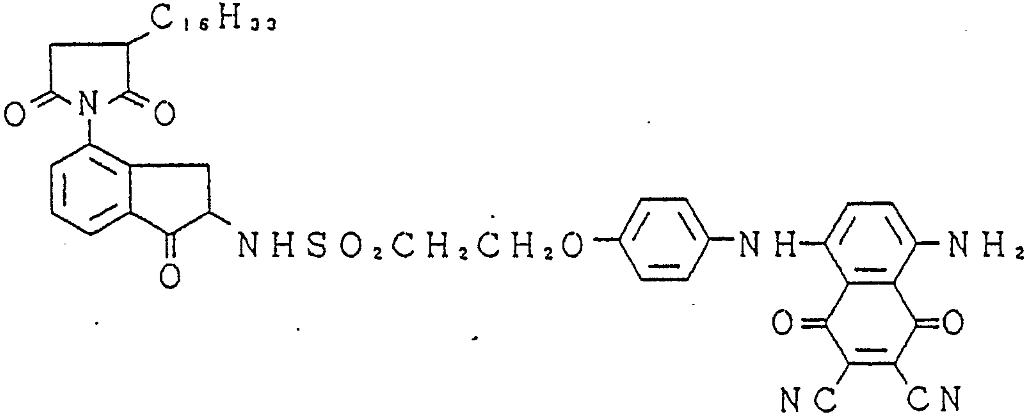
A − 4



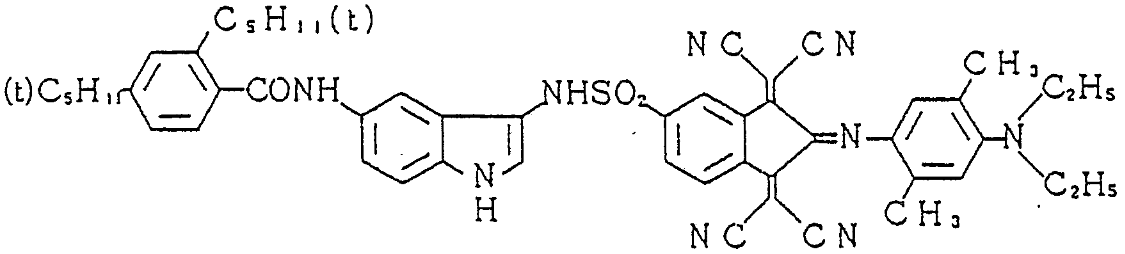
A − 5


OH
CON(C18H37)2
NSO2CH2CH2
N
C2H5
NH
CF3
OC2H5
O
O
NC
CN

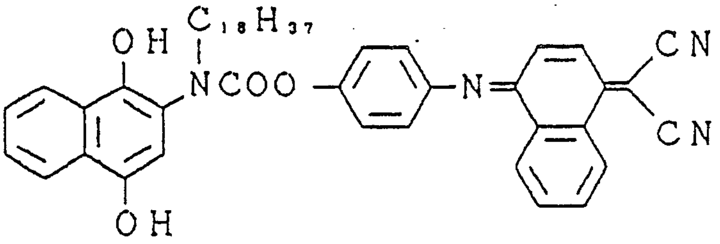
A − 6


C16H33
O
N
O
NHSO2CH2CH2O
NH
NH2
O
O
O
NC
CN

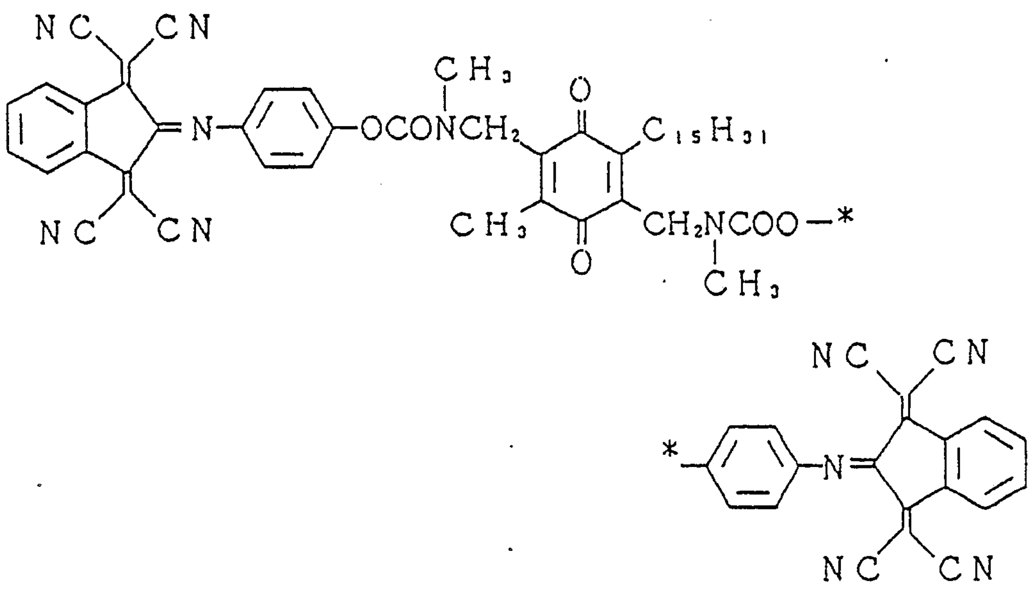
A − 7


C5H11(t)
(t)C5H11
CONH
NHSO2
N
H
NC
CN
NC
CN
N
CH3
CH3
C2H5
N
C2H5

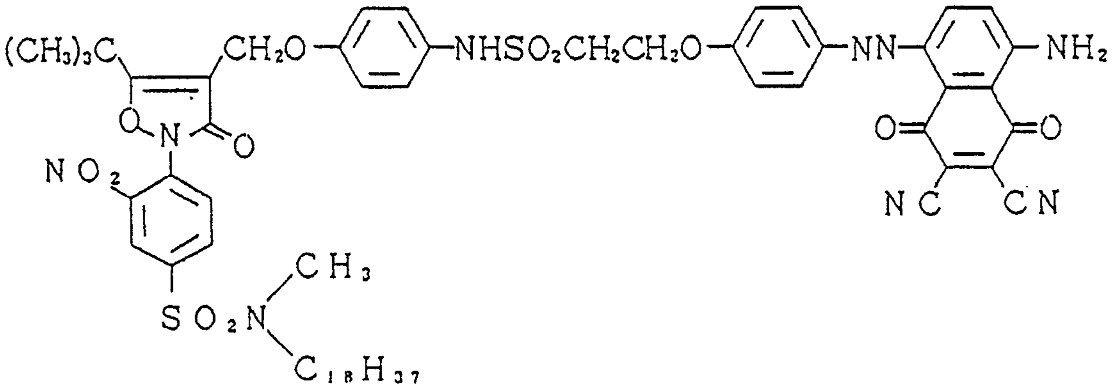
A − 8



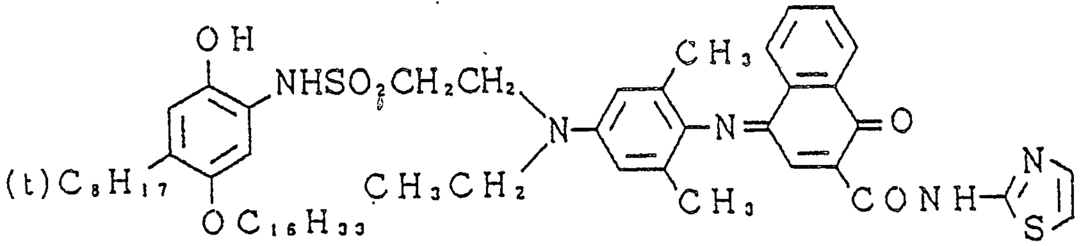
A − 9



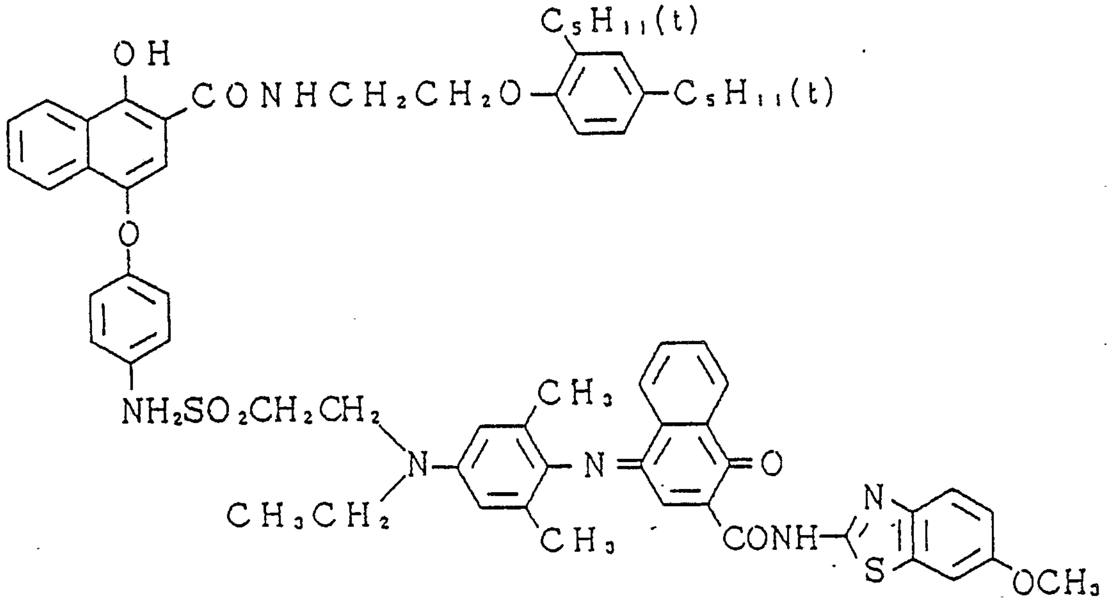
A − 10



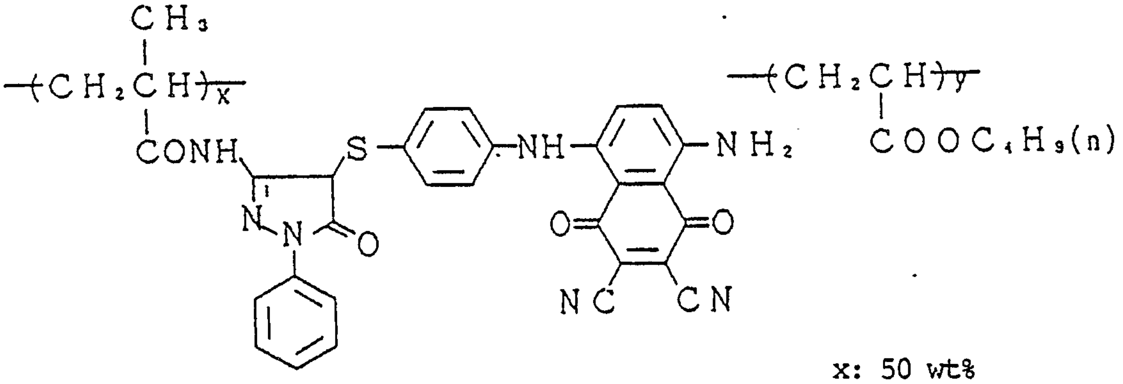
A-11



A-12



A-13



x: 50 wt%

y: 50 wt%

An amount added of an IR dye providing substance of the invention varies depending on properties of a compound used as well as properties of a photosensitive material. A most appropriate amount added is determined so that the IR dye density of a resultant image is 0.3 or higher, preferably, 0.5 or higher in terms of reflection density with a 850 nm light source.

In the case of a compound represented by Formula (1) or (2), a preferred amount added is 0.005 to 50 g, in particular 0.1 to 10 g per square meter of a photosensitive material. Two or more IR dye providing substances of the invention may be combinedly used.

An IR dye providing substance is incorporated into a layer containing photosensitive silver halide or its adjacent layer. More specifically, an IR dye providing substance is incorporated into a layer having a cyan dye providing substance. An arbitrary method may be used for incorporating the similar material into such a layer, and as one example, the material is incorporated singly or in conjunction with a dye providing substance by a method for incorporating a dye providing substance described later.

The heat developing color photosensitive material of the invention contains a dye providing substance.

Preferred dye providing substance of the invention include couplers capable forming non-diffusible dyes, as described in Japanese Patent O.P.I. Publication Nos. 44737/1987, 129852/1987 and 169158/1987; leuco dyes described in U.S. Patent No. 475,441; and azo dyes used for a heat developing dye bleach process, as described in U.S. Patent No. 4,235,957. Particularly preferred similar materials are diffusible dye providing substances capable of forming or releasing diffusible dyes, and, more specifically, compounds capable of forming diffusible dyes upon coupling reaction.

The diffusion dye providing substances useful in embodying the invention are hereunder described.

A compound applicable as a diffusion dye providing compound is one which takes part in the reduction of the photosensitive silver halide and/or the organic salt which is added according to a specific requirement so that it can form or release a diffusible dye as a function of the reaction. Such diffusion dye-providing substance can be divided into two types by the reacting mode, one type being dye-providing substance of the negative type which react as a positive function, forming negative dye images where silver halides of the negative type are in use, the other type being dye-providing substances of the positive type which react as a negative function, forming positive dye images where silver halides of the negative type are in use.

Examples of the dye-providing substance of the negative type are the dye-releasing reductive compounds described in U.S. Patent Nos. 4,463,079 and 4,439,513 and Japanese Patent O.P.I. Publication Nos. 60434/1984, 65839/1984, 71046/1984, 87450/1984, 88730/1984, 123837/1984, 124329/1984, 165054/1984 and 164055/1984.

Examples of other negative type dye-providing substances are coupling-type dye-releasing compounds described, for example, in U.S. Patent No. 4,474,867, Japanese Patent O.P.I. Publication Nos. 12431/1984. 48765/1984, 174834/1984, 776642/1984, 159159/1984 and 231040/1984.

Among coupling-type dye-forming compounds, those particularly preferable as a negative dye-providing substance are represented by the following Formula (x).

Formula (x)

$\mathrm{Cp}-(\mathrm{J})-(\mathrm{B})$

In this formula, Cp represents an organic group which is capable of forming a diffusible dye by reacting (coupling) with an oxidation product of a reducing agent; J represents a bivalent bonding group present as a substituent group on the active site of a coupler; B denotes a ballast group, which substantially virtually prevents a dye-providing substance from being diffused during the heat-developing process, examples of the ballast group being a sulfo group or the like whose molecular properties allow this effect and a group (a group having a large carbon number) whose size provides this effect. The coupler residue represented by Cp should preferably be one with a molecular weight under 700, especially preferably under 500, in order to make the dye formed assume a good diffusibility.

The preferred ballast group is a group having 8 or more, in particularly, 12 or more carbon atoms, or a sulfo group. More satisfactory is the use of a group containing both a sulfo group and a group with a large carbon number as above, and most satisfactory is the use of a ballast group which consists of a polymer chain.

Such a dye-forming compound of the coupling type containing a polymer chain group should preferably be one containing as a ballast group a polymer chain which consists of repetitive units derived from a monomer as represented by Formula (y)

Formula (y)

$\mathrm{Cp}-(\mathrm{J})-(\mathrm{Y})_{\ell}-(\mathrm{Z})-(\mathrm{L})$

Cp and J are synonymous with those in Formula (x); Y represents an alkylene group, an arylene group or an aralkylene group; and ℓ denotes 0 or 1, Z a bivalent organic group; and L an ethylenic unsaturated group or a group containing an ethylenic unsaturated group.

Examples of the dye-forming compounds of the coupling type represented by Formulas (x) and (y) are described in Japanese Patent O.P.I. Publication Nos. 124339/1984, 181345/1984, 2950/1985, 57943/1986 and 59336/1986 and U.S. Patent Nos. 4,631,251, 4,650,748 and 4,656,124, especially the dye-providing substances of the polymer type in the last-mentioned three U.S. Patents being preferable.

Examples of the positive-type dye-providing substance include dye-developing compounds described in Japanese Patent O.P.I. Publication Nos. 55430/1984 and 165054/1984; compounds which release diffusible dyes by intramolecular nucleophilic reactions, such as those in Japanese Patent O.P.I. Publication Nos.

154445/1984 and 766954/1984; cobalt-complex compounds, such as those in Japanese Patent O.P.I. Publication No. 116655/1984; and compounds which are rendered unable to release dyes when oxidized, such as those in Japanese Patent O.P.I. Publication Nos. 124327/1984 and 152440/1984.

A residue of a diffusible dye obtainable from a dye-providing substance of the invention preferably has a molecular weight of 800 or less, in particular, 600 or less, in order to improve the diffusibility of the dye, and the examples of which are residues of an azo dye, an azomethine dye, an anthraquinone dye, a naphthoquinone dye, a styryl dye, a nitro dye, a quinoline dye, a carbonyl dye, and a phthalocyanine dye. These dye residues may temporarily take a shortwave configuration provided their intended colors are restored during heat developing or transferring. To improve light fastness of image, it is one preferable mode of the invention that these dye residues are chelating-capable dye residues described in such as Japanese Patent O.P.I. Publication Nos. 48765/1984 and 124337/75.

These dye-providing substances may be used either singly or in combination of two or more. An amount of these substances added is not limited to a specific scope, but varies depending on a type of a dye-providing substance, or whether similar substances are used singly or combinedly, or the photographic structural layer of the sensitive material of the invention is single-layered or multilayered. One example of the amount added is 0.005 to 50 g, or, preferably, 0.1 to 10 g per square meter of a photosensitive material.

A method for incorporating a dye-providing substance of the invention into the photographic structural layer of the heat developing photosensitive material is not limited to a specific scope, and the examples of which are as follows: a similar substance is dissolved in a low boiling point solvent (e.g. methanol, ethanol and ethyl acetate) or a high boiling point solvent (e.g. dibutylphthalate, dioctylphthalate and tricersylphosphate), and is subjected to ultrasonic dispersing, and then incorporated into a photographic emulsion; a similar substance is dissolved in an aqueous alkali solution (e.g. 10% aqueous sodium hydroxide solution), and then the resultant mixture is neutralized with an acid (e.g. citric acid and nitric acid), and then incorporated into a photographic emulsion; a similar substance and an aqueous solution of an arbitrary polymer (e.g. gelatin, polyvinyl butyral and polyvinyl pyrolidone) are dispersed in a ball mill, and then incorporated into a photographic emulsion.

Next, the photosensitive silver halide useful in the invention is hereunder described. The silver halide used is arbitrarily selected, for example, silver chloride, silver bormide, silver iodide, silver bromochloride, silver chloroiodide and silver iodobromide. The photosensitive silver halide is obtained by an arbitrary method commonly used in the photographic art, such as a single jet precipitation process. According to one preferred mode of embodying the present invention, a useful silver halide emulsion used has core-type silver halide grains.

Another useful photographic emulsion is one having multilayer grains whose surface silver halide composition differs from that of cores. One example of this type of grains is core/shell silver halide grains, where silver halide composition may vary stepwise or continuously.

The crystal configurations of grains may or may not be clearly-defined ones, such as cubic, spherical, octahedral, dodecahedral and tetradecahedral crystals. Such a type of silver halide is described, for example, in Japanese Patent O.P.I. Publication No. 215948/1985.

Another type of a useful silver halide emulsion contains tabular silver halide grains of an aspect ratio (ratio of the diameter of grains to thickness) not less than 5:1, where individual grains have two mutually parallel crystal faces whose areas are larger than the area of other single crystals in such individual grains; the examples of such grains are described in Japanese Patent O.P.I. Publication Nos. 111933/1983, 111934/11983 and 108526/1983, and Research Disclosure No. 22534.

Still another type of a useful silver halide emulsion is one containing internal image type silver halide grains whose individual surface not fogged in advance. The non-prefogged internal image type silver halide is described, for example, in U.S. Patent Nos. 2,592,250, 3,206,313, 3,317,322, 3,511,622, 3,447,927, 3,761,266, 3,703,584 and 3,736,140. These types of silver halide grains are similar grains, as described in these patent specification, whose sensitivity at the core region is higher than that of the surface region. Other useful silver halide emulsions are as follows: a silver halide emulsion having silver halide grains containing multivalent metal ions that are described in U.S. Patent Nos. 3,271,157, 3,447,927 and 3,531,291; a silver halide emulsion having silver halide grains that contains a doping agent as described in U.S. Patent No. 3,761,276, wherein the surface of individual grains is subjected to weak chemical sensitization; a silver halide emulsion containing multilayered grains as described in Japanese Patent O.P.I. Publication Nos. 8524/1975 and 38525/1975; and silver halide emulsions described in Japanese Patent O.P.I. Publication Nos. 156614/1977 and 127549/1980.

These photosensitive silver halide emulsions may be chemically sensitized by an arbitrary method known in the photographic art.

The silver halide in each of the above-mentioned photosensitive emulsions can be either coarse or fine grains; however, a preferable grain sizes range from about 0.001 to about 1.5 µm, or, particularly, about 0.01 to 0.5 µm.

In another preparation method for a silver halide emulsion according to the invention, a photosensitive silver halide component is allowed to be coexistent with an organic silver salt described later, so that a portion of the organic silver salt forms photosensitive silver halide.

A photosensitive silver halide and the components to form a photosensitive silver salt can be used in variously different modes of combination. An amount of these silver halide and components being used for one layer is preferably 0.001 to 50 g, or, in particular, 0.1 to 10 g per square meter of a support.

Typical spectral sensitizing dyes used in the invention include cyanine, merocyanine, complex (trinuclear or tetranuclear) cyanine, holopolar cyanine, styryl, hemincyanine and oxonol.

An amount of such a sensitizing dye being added is 1×10^{-4} to 1 mol, or, preferably, 1×10^{-4} to 1×10^{-1} mol per mol of photosensitive silver halide or per mol of silver halide components.

A sensitizing dye is added at any step during the silver halide emulsion preparation. In other words, such a step is arbitrarily selected from the formation of silver halide grains, the removal of soluble salts; before, during and after the chemical sensitization.

The heat developing color photosensitive material of the invention may incorporate, according to a specific requirement, various organic silver salts in order to increase sensitivity and developability.

Examples of the organic silver salts that may be added to the heat developing color photosensitive material of the invention are described in Japanese Patent O.P.I. Publication Nos. 4921/1978, 52626/1974, 141222/1977, 36224/1978, 37626/1978 and 37610/1978 and U.S. Patents Nos. 3,330,633, 3,794,496 and 4,105,451; these silver salts are those of long chain-aliphatic carboxylic acid, those of carboxylic acid having a heterocycle (i.e. silver laurate, silver myristate, silver palmitate, silver stearate, silver arachidonate, silver behenate, silver α-(1-phenyltetrazolthio)acetate, and aromatic silver carboxylic acid silver (i.e. silver benzoate and silver phthalate). Other examples include silver salts of imino groups, such as the ones described in Japanese Patent Examined Publication Nos. 26582/1969, 12700/1970, 18416/1970 and 22185/1970, Japanese Patent O.P.I. Publication Nos. 137321/1977, 118638/1983 and 118639/1983 and U.S. Patent No. 4,123,274.

Other examples include silver complex compounds with stability constants in a range of 4.5 to 10.0, such as those described in Japanese Patent O.P.I. Publication No. 31728/1977, and silver salts of imizolinthione in U.S. Patent No. 4,168,980.

Of all the organic silver salts mentioned above, those preferable in the present invention are imino-group based silver salts, especially, silver salts of benzotriazol derivatives, or, more specifically, silver salts of 5-methylbenzotriazol and its derivatives, those of sulfobenzotriazol and its derivatives, and those of N-alkylsulfamoylbenzotriazol and its derivatives.

The organic silver salts according to the invention may be used singly or in combination. A silver salt may be prepared in a relevant binder, and then the resultant silver salt may be used without being isolated from the binder. Otherwise, isolated silver salt may be dispersed in a binder by appropriate means, thereby the dispersion is used. Useful means for dispersion include a ball mill, a sand mill, a colloid mill and a vibration mill, while these means are not mandatory.

In a usual preparation method for organic silver salt, silver nitrate and a relevant organic compound are dissolved in water or an organic solvent to provide a mixture solution. However, according to a specific requirement, it is useful that a binder or alkali such as sodium hydroxide be added in order to readily dissolve the organic solvent, or, otherwise, an ammonia silver nitrate solution may be used.

An amount of an organic silver salt used is preferably 0.01 to 500 mol, in particular, 0.1 to 100 mol, or, more specifically, 0.3 to 30 mol per mol of photosensitive silver halide..

A reducing agent possibly added to a heat developing color photosensitive material of the invention (in the discussion in this specification, a reducing agent precursor is included in the scope of reducing agents) is a similar agent usually used in the field of the heat developing photosensitive material.

Examples of reducing agents applicable to this invention are p-phenylenediamine-series and p-aminophenol-series developing agents, phosphoroamidophenol-series and sulfonamidoaniline-series developing agents, hydrazone-series color developing agents and their precursors, phenols, sulfonamidophenols, polyhydroxybenzenes, naphthols, hydroxybinaphthyls, methylenebisnaphthols, methylenebisphenols, ascorbic acid, 3-pyrazolidones, and pyrazolones, and relevant descriptions are found, for example, in U.S. Patent Nos. 3,531,286, 3,761,270 and 3,764,328, RD Nos. 12146, 15108 and 15127, Japanese Patent O.P.I. Publication No. 27132/1981, U.S. Patent Nos. 3,342,599 and 3,719,492, and Japanese Patent O.P.I. Publication Nos. 135628/1978 and 79035/1982.

The particularly preferred reducing agents are N-(p-N,N-dialkyl)aminophenylsulfamic acid salts described in Japanese Patent O.P.I. Publication Nos. 146133/1981 and 227141/1987.

Two or more of the above-mentioned reducing agents may be used simultaneously.

An amount added of the reducing agent above used in the heat developing color photosensitive material of the invention varies depending on a type of a photosensitive silver halide used, a type of organic silver salt and types of other additives. A most appropriate amount of the reducing agent added is preferably 0.01 to 1500 mol, in particular, 0.1 to 200 mol per mol photosensitive silver halide.

Examples of a binder possibly incorporated into the heat developing color photosensitive material of the invention include include synthetic or natural high molecular materials such as polyvinyl butyral, polyvinylacetate, ethyl cellulose, polymethyl methacrylate, cellulose acetate butyrate, polyvinyl alcohol, polyvinyl pyrolidone, gelatin, gelatin derivative such as phthalated gelatin, cellulose derivative, protein, starch, gum arabic. These examples are used singly or in combination. The particularly preferable are combined use of gelatin or a derivative thereof and a hydrophilic polymer such as polyvinyl pyrolidone or polyvinyl alcohol; in particular a mixture binder of gelatin and polyvinyl pyrolidone, as described in Japanese Patent O.P.I. Publication No. 229556/1984.

A preferred amount of a binder added is usually 0.05 to 50 g, in particular, 0.1 to 10 g per square meter support.

Additionally, a binder is preferably used at a rate of 0.1 to 10 g, in particular, 0.25 to 4 g per gram of dye providing substance.

The heat developing color photosensitive material of the invention is obtained by forming a photographic structural layer on a support. Examples of a useful support include polyethylene film, cellulose acetate film, and synthetic plastic films such as polyethylene terephthalate film and polyvinyl chloride; photographic paper; printing paper; paper supports such as baryta paper and resin-coated paper; and supports whose surface is coated with an electron-beam-setting resin composition that is set on any of the above-mentioned supports.

The heat developing color photosensitive material of the invention and/or an image receiving member used in the invention preferably contain various heat-solvents. A heat solvent is a compound that promotes heat developing and/or heat transferring. Examples of this compound as an organic polar compound are described in U.S. Patent Nos. 3,347,675 and 3,667,959, and RD (Research Disclosure) No. 17643 (XII), Japanese Patent O.P.I. Publication Nos. 229556/1984, 68730/1984, 84236/1984, 191251/1985, 232547/1985, 14241/1985, 52643/1986, 78553/1987, 42153/1987 and 44737/1987, U.S. Patent Nos. 3,438,776, 3,666,477 and 3,667,959, Japanese Patent O.P.I. Publication Nos. 19525/1976, 24829/1978, 60223/1978, 118640/1983 and 198038/1983. Among them, particularly advantageous in embodying the present invention include urea derivatives (e.g. dimethyl urea, diethyl urea and phenyl urea), amido derivatives (e.g. acetamide, benzamide, p-toluamide and p-butoxybenzamide), sulfonamide derivatives (e.g. benzenesulfonamide and α-toluene sulfonamide), multivalent alcohols (e.g. 1,5-pentandiol, 1,6-hexanediol, 1,2-cyclohexanediol, pentaerythritol and trimethylol ethane), and polyethylene glycols.

As a heat-solvent mentioned above, water-impermissible solid heat-solvents are further preferable. The water-impermissible solid heat-solvent in this specification means a compound which is solid at a normal temperatute and turns liquid at a higher temperature (60° or higher, or, preferably, 100°C or higher, in particular, 130°C or higher, 250°C or lower), and whose inorganicity/organicity ratio ("Schematics of Inorganicity", Yoshie Kohda, Sankyo Shuppan Co., Ltd., 1984) is 0.5 to 3.0, or, preferably, 0.7 to 2.5, in particular, 1.0 to 2.0.

Typical examples of the water-impermissible compound are described in Japanese Patent Application Nos. 136645/1987 and 139549/1987.

Layers that incorporate a heat-solvent include a photosensitive silver halide emulsion layer, an intermediate layer, a protective layer, and an image receiving layer of an image receiving member. The heat-solvent is added to a layer in a manner that positively allows effect of the layer.

A preferred amount of addition of a heat-solvent is 10 to 500 wt%, or, preferably, 30 to 200 wt% of an amount of binder.

The previously mentioned organic silver salt and the above-mentioned heat-solvent may be added in a same dispersion system. A binder, a dispersion medium and a dispersion apparatus used may be same as those for individually preparing the organic silver salt dispersion and the heat-solvent dispersion.

The heat developing color photosensitive material of the invention may contain various additives according to a specific requirement, other than the above-mentioned various components.

The heat developing color photosensitive material of the invention may contain a compound which is known as a tone adjuster in the field of the heat developing photosensitive material, so as to allow it serve as a development accelerator. Examples of a tone adjuster are compounds described in Japanese Patent O.P.I. Publication Nos. 4928/1971, 6077/1971, 5019/1974, 5020/1974, 95215/1974, 107727/1974, 2524/1975, 67132/1974, 67641/1975, 114217/1975, 33722/1977, 99813/1977, 1020/1978, 55115/1978, 76020/1978, 125014/1978, 156523/1979, 156524/1979, 156525/1979, 156526/1979, 4060/1980, 4061/1980 and 32015/1980, West German Patent Nos. 2,140,406, 2,141,063 and 2,220,618, U.S. Patent Nos. 3,847,612, 3,782,941 and 4,201,582, and Japanese Patent O.P.I. Publication Nos. 207244/1982, 207245/1982, 1896328/1983 and 193541/1983.

Other development accelerators are compounds described in Japanese Patent O.P.I. Publication Nos. 177550/1984 and 111636/1984. Also useful are development accelerator releasing compounds described in Japanese Patent O.P.I. Publication No. 159642/1986.

Useful anti-fogging agents are as follows: higher aliphatic acids described in U.S. Patent No. 3,645,739; mercuric salts described in Japanese Patent Examined Publication No. 11113/1972; N-halogen compounds described in Japanese Patent O.P.I. Publication No. 47419/1976; mercapto compound-releasing compounds described in U.S. Patent No. 3,700,457 and Japanese Patent O.P.I. Publication No. 50725/1976; arylsulfonic acids described in Japanese Patent O.P.I. Publication No. 125016/1974; lithium carboxylate salts described in Japanese Patent O.P.I. Publication No. 47419/1976; oxidizing agents described in British Patent No. 1,455,271 and Japanese Patent O.P.I. Publication No. 101019/1975; sulfinic acids and thiosulfonic acids described in Japanese Patent O.P.I. Publication No. 19825/1978; 2-thiouracils described in Japanese Patent O.P.I. Publication No. 3223/1976; element sulfur described in Japanese Patent O.P.I. Publication No. 26019/1976; disulfide or polysulfide compounds described in Japanese Patent O.P.I. Publication Nos. 42529/1976, 81124/1976 and 93149/1980; rosins and diterpenes described in Japanese Patent O.P.I. Publication No. 57435/1976; polymeric acids containing free carboxyl or sulfonic acid group, and described in Japanese Patent O.P.I. Publication No. 104338/1976; thiazolinethiones described in U.S. Patent No. 4,138,265; 1,2,4-triazoles or 5-mercapto-1,2,4-triazoles described in Japanese Patent O.P.I. Publication No. 51821/1979 and U.S. Patent No. 4,137,079; thiosulfinic esters described in Japanese Patent O.P.I. Publication No. 140883/1980; 1,2,3,4-thiatriazoles described in Japanese Patent O.P.I. Publication No. 142331/1980; dihalgen or trihalogen compounds described in Japanese Patent O.P.I. Publication Nos. 46641/1984, 57233/1984 and 57234/1984; thiol compounds described in Japanese Patent O.P.I. Publication No. 111636/1984; hydroquinone derivatives described in Japanese Patent O.P.I. Publication No. 198540/1985; and combined used of hydroquinone derivative and benzotriazole derivative as described in Japanese Patent O.P.I. Publication No. 227255/1985.

Other particularly preferred anti-fogging agents that may be used in conjunction with the above-mentioned similar agents are as follows: inhibitors having a hydrophilic group as described in Japanese Patent O.P.I. Publication No. 78554/1987; polymeric inhibitors described in Japanese Patent O.P.I. Publication No. 121452/1987; and inhibitors having a ballast group as described in Japanese Patent O.P.I. Publication No. 123456/1987.

The photosensitive material of the invention may further incorporate an inorganic or organic alkali, or an alkali precursor. Examples of such a precursor are compounds (e.g. guanidinium trichloroacetate) that release alkaline materials by decarbonization with heating and compounds that release amines by reaction such as intramolecular nucleophilic substitution reaction; these examples include alkali-releasing agents described in Japanese Patent O.P.I. Publication Nos. 130745/1981 and 132332/1981, British Patent No. 2,079,480, U.S. Patent No. 4,060,420, Japanese Patent O.P.I. Publication Nos. 157637/1984, 166943/1984, 180537/1984, 174830/1984 and 195237/1984.

The photosensitive material of the invention may further incorporate, according to a specific requirement, various additives such as an antihalation dye, a fluorescent brightening agent, a hardener, an antistatic agent, a plasticizer, a spreading agent, a matting agent, a surfactant, and an anti-fading agent, and the examples of which are described in RD Vol. 170, June 1978, No. 17029 and in Japanese Patent O.P.I. Publication No. 135825/1987.

The heat developing color photosensitive material of the invention contains (a) photosensitive silver halide, (b) a reducing agent and (c) a dye providing substance. The material preferably contains, according to a specific requirement, (d) a binder and (e) organic silver. These components may be contained in one single heat developing photosensitive layer, or otherwise, not necessarily be contained in one single photographic structural layer. A heat developing photosensitive layer may be divided into two independent layers, thereby one layer contains the components (a), (b), (d) and (e), while in the other adjacent heat developing photosensitive layer contains a dye providing substance (c). These components may be divided into two or more groups which are independently added to two or more photographic structural layers, as far as these components can react with each other.

The heat developing photosensitive layer may be divided into two layers; for example, a low sensitivity layer and a high sensitivity layer; or a high density layer and a low density layer. The layer may be divided into more layers.

The heat developing color photosensitive material of the invention has one or more heat developing photosensitive layers. In the case of a full-color photosensitive material, the similar material of the invention usually comprises three heat developing photosensitive layers each sensitive to a different color, wherein in each photosensitive layer, a dye of a different hue is formed or released by heat developing.

Usually, a blue-sensitive layer contains a yellow dye; a green-sensitive layer contains a magenta dye; and a red-sensitive layer contains a cyan dye; however, this arrangement is not mandatory. It is also possible to incorporate a near-IR-sensitive layer.

Arrangement of the respective layers is arbitrarily selected in accordance with a nature of photographic application; one arrangement comprises a support sequentially provided thereon a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer; another arrangement comprises a support sequentially provided thereon a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer; still another arrangement comprises a support sequentially provided thereon a green-sensitive layer, a red-sensitive layer and a blue-sensitive layer.

Other than the heat developing photosensitive layer, the heat developing photosensitive layer of the invention may comprise non-photosensitive layers such as a subbing layer, an intermediate layer, a protective layer, a filter layer, a backing layer and a peeling layer. For forming the heat developing photosensitive layer as well as these non-photosensitive layers on the support by coating, a method used is similar to that for a conventional silver halide photosensitive material.

Once imagewise exposing is complete, the heat developing color photosensitive material of the invention is developed by simply heating it preferably at 80 to 200° C, in particular, 100 to 170° C, preferably for 1 to 180 seconds, in particular 1.5 to 120 seconds. Transferring a diffusible dye onto an image receiving layer may be performed, at the same time as heat developing, by contacting the image receiving member with the photosensitive side of the photosensitive material during heat developing. Otherwise, transferring may be performed after heat developing, by contacting the photosensitive material with an image receiving member, or by contacting both the materials after feeding water between them and, if necessary, by heating. Additionally, preheating may be performed at 70 to 180° C prior to exposing. In order to ensure close contact between both the materials, both materials may be preheated at 80 to 250° c immediately before heat developing/transferring, as described in Japanese Patent O.P.I. Publication No. 143338/1985 and Japanese Patent Application No. 3644/1985.

The heat developing color photosensitive material of the invention may be subjected to various heating means.

Every heating means for a conventional heat developing photosensitive material is applicable to such heating means, and examples of which are as follows: a photosensitive material is contacted with a heated block or plate, or with a heat roller or heat drum; or is allowed to pass through a high temperature atmosphere, or subjected to heating with high frequency radiation; or otherwise, an electroconductive layer containing an electroconductive material such as carbon black is disposed on the rear face of the photosensitive material of the invention or on the rear face of a heat-transferring type image receiving member, whereby heating-induced Joule's heat is utilized. A pattern for heating is not limited to a specific scope; the similar materials may be preheated and then reheated; they may be subjected to a high temperature for a short period or to a low temperature for a long period; they may be continuously heated for a long period from a low temperature and then continuously cooled, wherein this sequence may be repeated; or they may be heated intermittently. However, a simple heating pattern is preferable. Exposing and heating may be performed simultaneously.

An image receiving layer useful in an image receiving member of the invention is one capable of receiving a dye that is released or formed in the heat developing photosensitive layer by heat developing, and preferred such a layer contains a polymer that contains tertiary or quaternary ammonium salt and is described in U.S. Patent No. 3,709,690. A typical image receiving layer relevant to diffusion transfer process is obtained by coating a support with a mixture comprising polymer containing ammonium salt and tertiary amine, as well as gelatin and polyvinyl alcohol. Other useful dye receiving substance include heat resistant organic high molecular materials, described in Japanese Patent O.P.I. Publication No. 207250/1982, whose glass transition point being higher than 40° C and lower than 250° C.

These polymers may be carried as an image receiving layer by a support, or may serve as a support.

Examples of the above-mentioned heat-resistant high molecular material include polystyrene, polystyrene derivative having a substituent that has 4 or less carbon atoms, polyvinylcyclohexane, polydivinyl benzene, polyvinyl pyrrolidone, polyvinyl carbazole, polyallyl benzene, polyvinyl alcohol; polyacetals such as polyvinyl formal and polyvinyl butyral; polyvinyl chloride, chlorinated polyethylene, polytrichlorofluoroethylene, polyacrylonitrile, poly-N,N-dimethylacrylamide; polyacrylate having p-cyanophenyl group, pentachlorophenyl group or 2,4-dichlorophenyl group; polyesters such as polyacrylchloro acrylate, polymethyl methacrylate, polyethyl methacrylate, polypropyl methacrylate, polyisopropyl methacrylate, polyisobutyl methacrylate, poly-tert-butyl methacrylate, polycyclohexyl methacrylate, polyethylene glycol dimethacrylate, poly-2-cyano-ethyl methacrylate and polyethylene terephthalate; polysulfone, polycarbonate such as Bisphenol A; polyanhydride, polyamide and cellulose acetate. Other useful polymers are synthetic polymers whose glass transition point of 40 °C or higher, as exemplified in "Polymer Handbook", 2nd ed. (J. Brandrup, E.H. Immergut), published from John Wiley & Sons. Usually, a molecular weight of such high molecular compounds is preferably 2000 to 200000. These high molecular compounds may be used singly or as a blend of two or more; or two or more materials may be combined to form a useful copolymer.

Particularly preferred image receiving layers include a polyvinyl chloride layer described in Japanese Patent O.P.I. Publication No. 223425/1984, and a polycarbonate layer described in Japanese Patent O.P.I. Publication No. 19138/1985.

These polymers can be used as a support cum image receiving layer (image receiving member); in this case, the support may be single-layered or multilayered.

A useful support for image receiving member is arbitrarily selected from a transparent support, an opaque support and the like. Typical examples of a useful support include films made of polyethylene terephthalate, polycarbonate, polystyrene, polyvinyl chloride, polyethylene and polypropylene; and similar supports containing a dye such as titanium oxide, barium sulfate, calcium carbonate and talc; baryta paper; RC paper made of paper laminated with a thermoplastic resin containing a dye; cloth, glass; metal sheets such as of aluminum; support prepared by coating any of the above-mentioned supports with an electron-beam setting resin composition that is set thereon; and support provided with a coating layer containing a dye. Another useful support is a cast coat paper described in Japanese Patent Application No. 126972/1986.

There are other useful supports i.e. a paper-support coated with an electron-beam setting resin composition that is set thereon, and a paper-support disposed thereon a dye-coating layer, and the dye-coating layer is coated with an electron-beam setting resin composition that is set thereon: since the resin layer without further modification serves as an image receiving layer, these supports can be used as an image receiving member without any modification.

The heat developing color photosensitive material of the invention may be the so-called "mono-sheet type heat developing photosensitive material" described in Research Disclosure No. 15108, Japanese Patent O.P.I. Publication Nos. 198458/1982, 207250/1982 and 80148/1986, wherein a photosensitive layer and an image receiving layer are disposed on one single support.

The heat developing color photosensitive material of the invention preferably has a protective layer into which a compound of the invention is preferably incorporated.

The protective layer may contain various additives commonly used in the photographic art. Such additives include various matting agents, colloidal silica, a lubricant, an organic fluoro compound (especially, a fluorine based surfactant), an antistatic agent, an UV absorvent, a high boiling point organic solvent, an oxidation inhibitor, a hydroquinone derivative, a polymer latex, a surfactant (including a high molecular surfactant), a hardener (including a high molecular hardener), organic silver salt grains, and non-photosensitive silver halide grains.

These additives are described in Research Disclosure Vol. 170, June 1978, No. 17029 and in Japanese Patent O.P.I. Publication No. 135825/1987.

EXAMPLES

Typical examples of the present invention are hereunder described. However, it should be noted that these examples by no means limit the scope of the invention.

Example 1

In this example, a silver iodobromide emulsion, a dispersion having an organic silver salt and a heat-solvent, a dye-providing substance dispersion and a reducing-agent dispersion were prepared in order to obtain a heat developing color photosensitive material. Additionally, an image receiving member was prepared in a manner described later.

(1) Preparation of silver iodobromide emulsion

At 50° C, using a blending machine described in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982, to Solution (A) comprising 20 g of ossein gelatin, 1000 mℓ of distilled water and ammonia were simultaneously added, while the pAg was maintained at a constant level, 500 mℓ of Solution (B) (aqueous solution) containing 11.6 g of potassium iodide and 131 g of potassium bromide, and 500 mℓ of Solution (C) (aqueous solution) containing 1 mol of silver nitride and ammonia.

The crystal configuration and size of grains in the emulsion prepared were controlled by regulating the pH, pAg, and the rate of adding Solutions (B) and (C). Thus a core emulsion was prepared, wherein the silver iodide content was 7 mol%, individual grains were regular octahedral crystals whose average grain size was 0.25 µm.

Next, based on the above-mentioned process, silver halide shell containing 1 mol% of silver iodide was formed on individual grains so as to prepare a core/shell silver halide emulsion, wherein individual grains were regular octahedral crystals whose average grain size was 0.3 µm (monodispersability being 9%). The so-obtained emulsion was rinsed with water, and subjected to desalination.

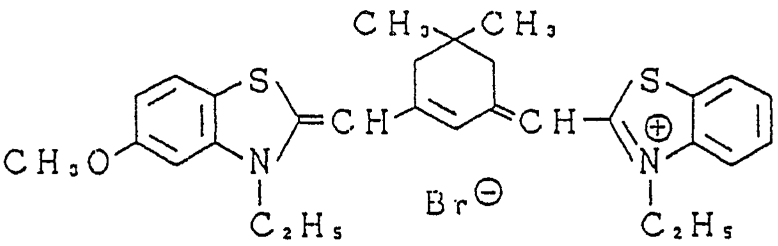
(2) (i) Preparation of photosensitive silver halide dispersions

To 700 mℓ of the so-prepared silver iodobromide emulsion were added the ingredients below, and the resultant emulsion was subjected to chemical sensitization and spectral sensitization, so as to obtain red-sensitive, green-sensitive and blue-sensitive silver halide dispersions.

(i) Preparation of red-sensitive silver iodobromide emulsion

Above-mentioned silver iodobromide emulsion	700 mℓ
4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.4 g
Gelatin	32 g
Sodium thiosulfate	10 mg
1% methanol solution of Sensitizing Dye (a) below	80 mℓ
Distilled water	1200 mℓ

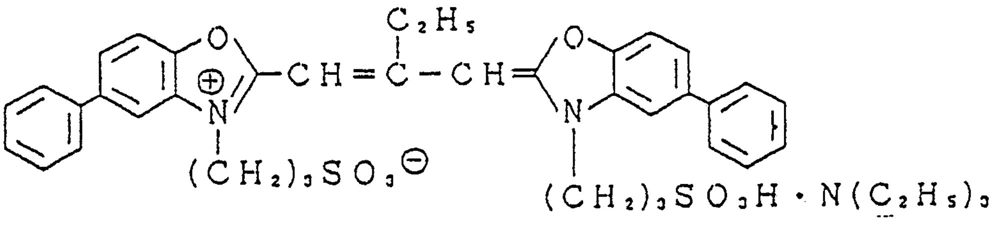
Sensitizing Dye (a)



(ii) Preparation of green-sensitive silver iodobromide emulsion

Above-mentioned silver iodobromide emulsion	700 mℓ
4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.4 g
Gelatin	32 g
Sodium thiosulfate	10 mg
1% methanol solution of Sensitizing Dye (b) below	80 mℓ
Distilled water	1200 mℓ

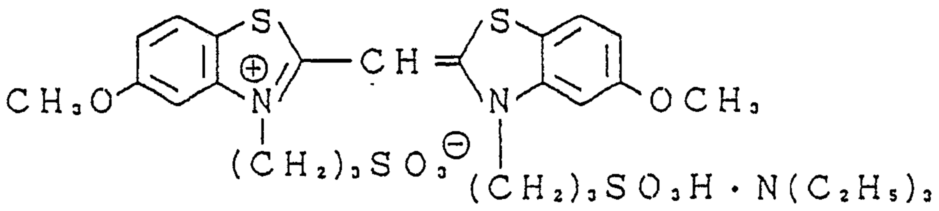
Sensitizing Dye (b)



(iii) Preparation of blue-sensitive silver iodobromide emulsion

Above-mentioned silver iodobromide emulsion	700 mℓ
4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.4 g
Gelatin	32 g
Sodium thiosulfate	10 mg
1% methanol solution of Sensitizing Dye (c) below	80 mℓ
Distilled water	1200 mℓ

Sensitizing Dye (c)



(3) Preparation of dispersion comprising organic silver salt and heat-solvent

Based on the prescription below, a dispersion comprising organic silver salt and heat-solvent was prepared.

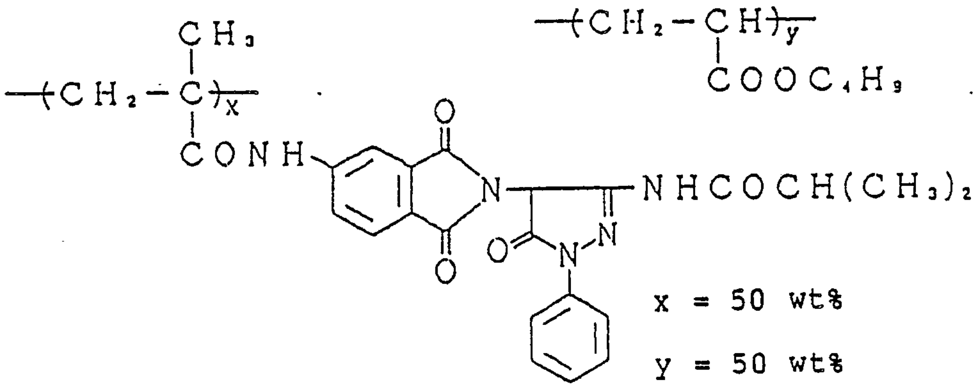
Prescription	
5-methylbenzotriazole silver p-tolylamide Polyvinyl pyrrolidone (10%)	60.5 g 346 g 446 mℓ
Water to	2000 g

The mixture was dispersed using an alumina ball mill, and then, the pH level was adjusted to 5.5 with 10% aqueous citric acid solution. Thus a dispersion comprising organic silver salt and a heat solvent was prepared.

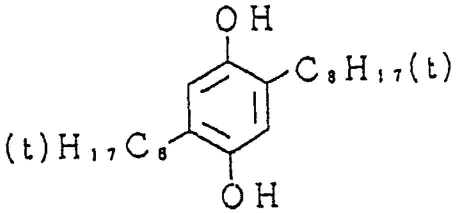
(4)-(1) Preparation of Dispersion 1 comprising dye-providing substance

35.5 g of high molecular a dye-providing substance (1) illustrated below and 5.0 g of hydroquinone compound illustrated below were dissolved in 200 mℓ of ethyl acetate, and the resultant mixture was blended with 720 mℓ of aqueous gelatin solution comprising 124 mℓ of 5 wt% aqueous Alkanol XC (DuPont) solution and 30.5 g of phenylcarbamoyl gelatin (Luthlaw, Type 17819PC), and the blend was dispersed with an ultrasonic homogenizer. Next, ethyl acetate was distilled out, and the pH was adjusted to 5.5 and the amount was adjusted to 795 mℓ. Thus Dispersion 1 comprising a dye providing substance was obtained.

High molecular dye-providing substance (1)

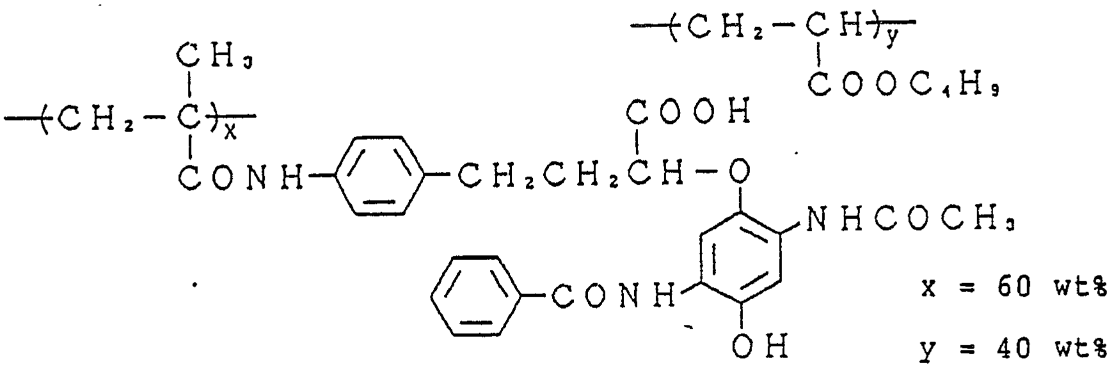


Hydroquinone compound



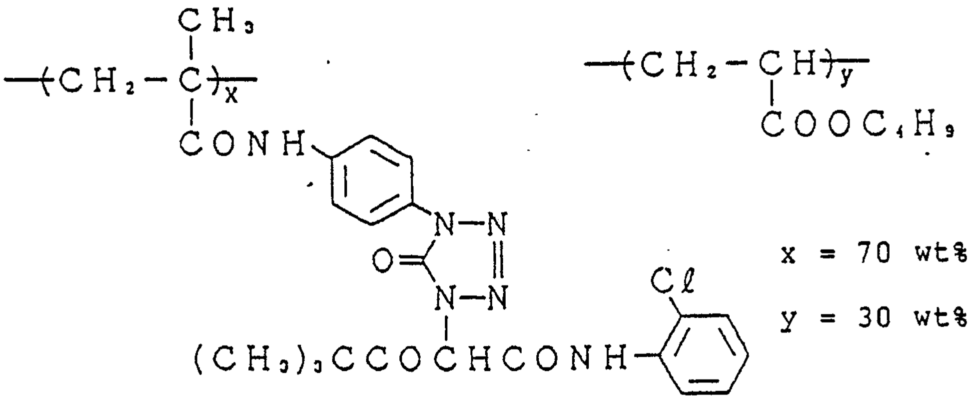
(4)-(2) Preparation of Dispersion 2 comprising dye-providing substance

Dispersion 2 comprising a dye-providing substance was obtained in a manner identical to that of Dispersion 1 comprising a dye-providing substance except that the dye-providing substance in Dispersion 1 was replaced with the following high molecular dye-providing substance (2).



(4)-(3) Preparation of Dispersion 3 comprising a dye-providing substance

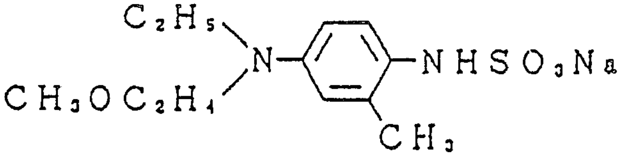
This dispersion was obtained in a manner identical to that of Dispersion 1 comprising a dye-providing substance except that the dye-providing substance in Dispersion 1 was replaced with the following high molecular dye-providing substance (3).



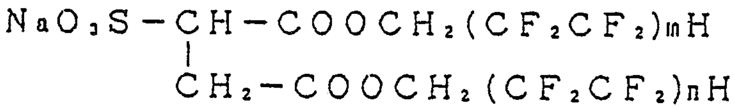
(5) Preparation of reducing agent solution

23.3 g of a reducing agent illustrated below, 14.6 g of poly(N-vinylpyrrolidone) and 0.50 g of a fulorine-based surfactant illustrated below were dissolved in water, and then the pH level was adjusted to 5.5. Thus 250 mℓ of reducing agent solution was prepared.

Reducing agent



Surfactant



$$\begin{array}{l} NaO_3S-CH-COOCH_2(CF_2CF_2)_mH \\ \qquad\qquad\;\; | \\ \qquad\qquad CH_2-COOCH_2(CF_2CF_2)_nH \end{array}$$

(m, n; 2 or 3)

(6) Preparation of heat developing color photosensitive material

Using the so-prepared dispersion comprising organic silver and heat-solvent, the silver halide emulsion, the dispersion comprising a dye-providing substance, and the reducing agent solution, a multilayered color photosensitive material (1) whose layers summarized in Table 1 was prepared.

Photosensitive materials (2) through (6) were prepared (types and amounts of compounds added are summarized in Table 1) in a manner identical to that of Photosensitive material (1) except that an IR coupler of the invention was added to the 6th layer of the photosensitive material.

Table 1

7th layer	Protective layer	Gelatin 0.71 g, phenylcarbamoyl gelatin 0.36 g, polyvinylpyrrolidone (K-30) 0.53 g, reducing agent 0.48 g, tricresylphosphate 0.2 g
6th layer	Blue-sensitive layer	5-methylbenzotriazole silver 2.5 g, reducing agent 1.2 g, tricresylphosphate 0.344 g, high-molecular dye-providing substance (2) 1.13 g, blue-sensitive silver halide emulsion 0.76 gAg, gelatin 1.22 g, phenylcarbamoyl gelatin 0.61 g, polyvinyl pyrolidone (K-30) 0.92 g, heat-solvent (p-toluamide) 4.89 g
5th layer	2nd intermediate layer	Gelatin 1.77 g, reducing agent 0.53 g, tricresylphosphate 0.22 g, yellow filter dye (F-1) 0.1 g
4th layer	Green-sensitive layer	5-methylbenzotriazole silver 0.8 g, reducing agent 0.675 g, tricresylphosphate 0.2 g, high-molecular dye-providing substance (1) 0.9 g, green-sensitive silver halide emulsion 0.457 gAg, gelatin 1.0 g, phenylcarbamoyl gelatin 0.5 g, polyvinyl pyrrolidone (K-30) 0.75 g, heat-solvent (p-toluamide) 4 g, butanetriol 0.25 g
3rd layer	1st intermediate layer	Gelatin 0.50 g, reducing agent 0.49 g, tricresylphosphate 0.2 g
2nd layer	Red-sensitive layer	5-methylbenzotriazole silver 1.6 g, reducing agent 0.8 g, tricresylphosphate 0.33 g, high-molecular dye-providing substance (3) 1.06 g, red-sensitive silver halide emulsion 0.68 gAg, gelatin 1.18 g, phenylcarbamoyl gelatin 0.59 g, polyvinyl pyrrolidone (K-30) 0.89 g, heat-solvent (p-tolumamide) 5.2 g
1st layer	Gelatin layer	Gelatin 2.5 g
Support		A 180 µm-thick transparent polyethylene terephthalate film having latex subbing layer

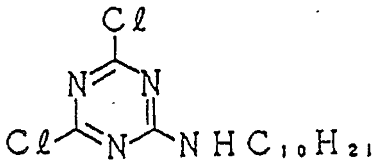
Each amount of addition is a coating weight per square meter.
(An amount of silver halide is indicated in a silver-converted amount.
Each layer contained trace amounts of surfactant and hardener.)

(7) Preparation of image receiving member

In tetrahydrofuran solution of polyvinyl chloride (n = 1,100, Wako Junyaku) were dissolved Compounds (A) and (B) illustrated later, and the resultant solution was applied to and dried on a photographic baryta paper so that the coating weight of polyvinyl chloride was 15.0 g/m^2, so as to obtain an image receiving member.

Blue-exposing light, green-exposing light, red-exposing light and white-exposing light each of 800 CMS were individually irradiated on each of the previously mentioned Heat Developing Color Photosensitive Materials (1) through (6) through an optical step wedge. Then each photosensitive material was placed on the image receiving member, thereby subjected to heat developing using a heat developing machine (Developer Module 277, 3M) for 90 sec. at 145° C. Immediately, each photosensitive material was peeled of the image receiving member, and, by using a photographic densitometer (PDA-65, Konica Corporation), each so-processed image receiving member was evaluated for reflective density of yellow (Y), magenta (M) and cyan (C) images, reflective density to IR light (850 nm). The resultant density maximum (D_{max}) and density minimum (D_{min}) (fog) of each dye image are summarized in Table 2.

Compound (A)



Coating weight; 750 mg/m^2

Compound (B)
$HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$
Coating weight; 600 mg/m^2

Table 2

Photosensitive material	IR coupler	Amount added	Y		M		C		IR
			Dmax	Dmin	Dmax	Dmin	Dmax	Dmin	Dmax
1 (Comparative)	-	-	1.84	0.13	2.19	0.16	2.41	0.14	0.0
2 (Invention)	IR- 7	0.4 g	1.82	0.12	2.17	0.14	2.02	0.10	0.53
3 (Invention)	IR-10	0.4 g	1.80	0.13	2.16	0.15	2.04	0.10	0.69
4 (Invention)	IR-13	0.4 g	1.83	0.12	2.18	0.15	2.01	0.10	1.08
5 (Invention)	IR-14	0.45g	1.85	0.13	2.17	0.16	2.06	0.11	1.11
6 (Invention)	IR-20	0.5 g	1.81	0.12	2.14	0.14	2.00	0.10	0.99
Amount added is coating weight per square meter.									

An IR image is usually found on blue-exposed and white-exposed regions. However, data of IR image in Table 2 is the reflective density measured, with IR light, on the density maximum region of an image (black) in a white-exposed region.

As can be understood from the results in Table 2, character data, signal data and color image data were read on a heat developing color photosensitive material of the invention, by means of light whose spectral being in a longer wavelength region than 750 nm.

Example 2

A multilayer photosensitive material (7) whose composition specified in Table 3 was prepared.

The obtained photosensitive material (7) was exposed through an optical step wedge with each of green light, red light and IR light, and then, the emulsion surface of the material was coated with water by a wire bar, and the photosensitive material was placed on Image-receiving member 2 specified later and was subjected to heat developing for 30 seconds at 130° C. On each image receiving member was formed a tranasferred image of cyan, magenta or yellow in correspondence with each exposing light.

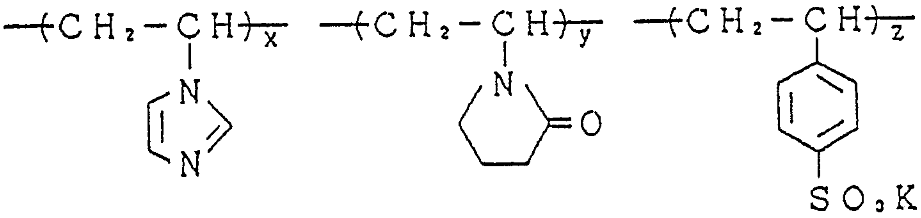
The reflective density of the cyan dye image was measured with IR light (850 nm). The resultant D_{max} was 1.48, while the D_{min} was 0.31.

Preparation of Image-receiving member 2

By coating, a lime-modified gelatin layer (coating weight, 2.3 g/m^2) was formed on a photographic baryta paper, and a dying layer of the following composition was formed by coating. Thus Image-receiving member 2 was obtained.

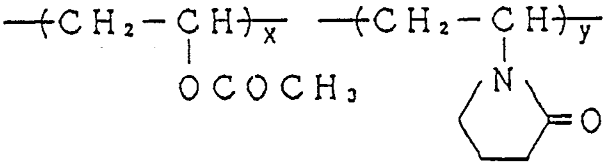
Composition of dying layer	
Polymer (I) illustrated below	4.25 g/m^2
Polymer (II) illustrated below	1.4 g/m^2
Lime-modified gelatin	3 g/m^2

Polymer (I)



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

Polymer (II)



x: 30 wt%

y: 70 wt%

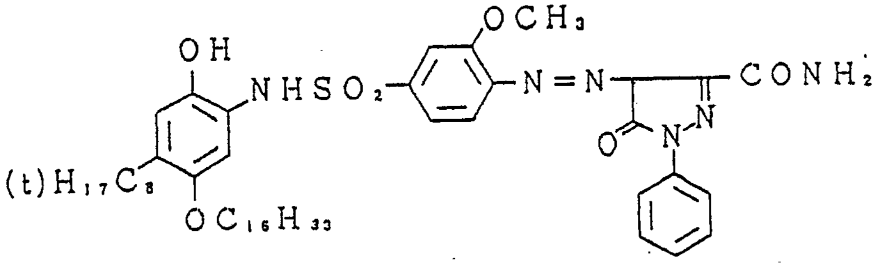
Other photosensitive materials were prepared by replacing IR-dye-providing substance A-1 of the invention with A-2, A-3 or A-4, and these photosensitive materials provided IR dye images similar to that of Photosensitive material (7). However, measurement with IR light taken on photosensitive materials that lacked an IR-dye-providing substance of the invention failed to detect an image.

Table 3

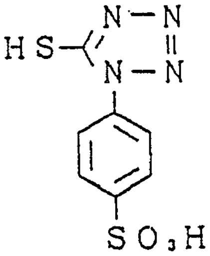
6th layer	Protective layer	Gelatin 1 g, guanidinetrichloroacetic acid 0.33 g, 0.4 μm silica 0.1 g
5th layer	Blue-sensitive emulsion layer	Benzotriazole silver 0.2 g, heat-solvent B *1) 0.2 g, green-sensitive silver halide 0.4 g (Ag), dye-providing substance (4) *2) 0.4 g, tricresylphosphate 0.8 g, gelatin 1 g, guanidinetrichloroacetic acid 0.33 g, inhibitor B *3) 0.01 g
4th layer	inter-mediate layer	Gelatin 1.2 g, guanidinetrichloroacetic acid 0.4 g
3rd layer	Red-sensitive emulsion layer	Benzotriazole silver 0.2 g, heat-solvent B *1) 0.2 g, red-sensitive silver halide 0.3 g (Ag), dye-providing substance (5) *4) 0.4 g, guanidinetrichloroacetic acid 0.33 g, gelatin 1 g, tricresylphosphate 0.6 g, inhibitor B *3) 0.01 g
2nd layer	Inter-mediate layer	Gelatin 1.0 g, guanidinetrichloroacetic acid 0.33 g
1st layer	IR-sensitive emulsion layer	Benzotriazole silver 0.3 g, heat-solvent B *1) 0.3 g, IR-sensitive silver halide *5) 0.45 gAg, dye-providing substance (6) *6) 0.3 g, IR-dye-providing substance of the invention (A-1) 0.2g, guanidinetrichloroacetic acid 0.5 g, gelatin 1.5 g, tricresylphosphate 0.8 g, inhibitor B 0.015 g
Support		A 180 μm-thick transparent polyethylene terephthalate film having latex subbing layer

*1) Heat-solvent B: benzenesulfonamide

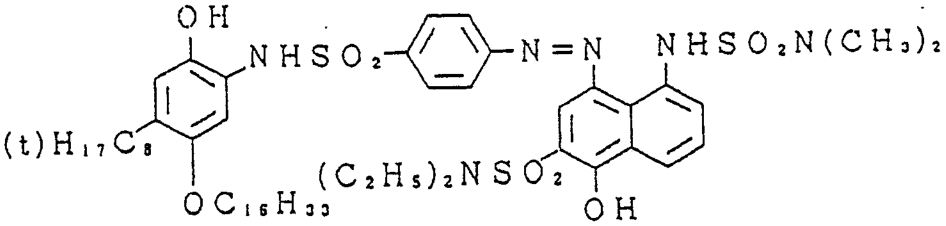
*2) Dye-providing substance (4):



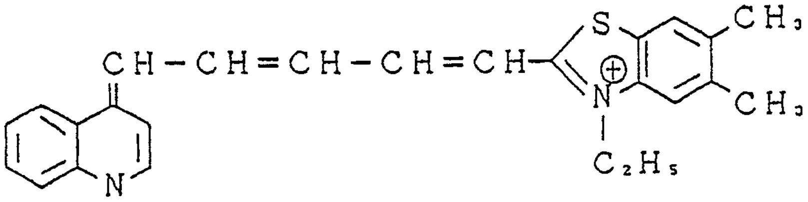
*3) Inhibitor B:



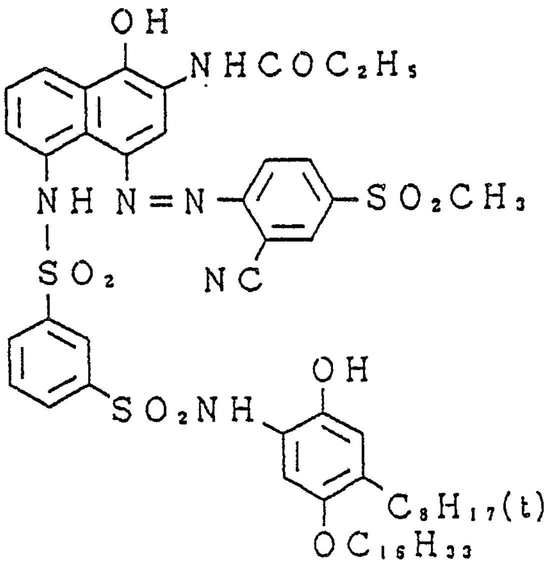
*4) Dye-providing substance (5):



*5) Sensitizing dye used:



*6) Dye-providing substance (6):



Example 3

Personal data, character data and color image data were written (by exposing) onto a photosensitive layer of Photosensitive material 5 of Example 1, by using blue (He-Cd), green (Ar) or red (He-Ne) gas laser.

For the exposing, the image was flipped around its longitudinal axis so that the finally obtained image is an mirror image when seen from the photosensitive layer side. Next, each photosensitive material undergone exposing was treated by a method same as in Example 1. Thus dye image was formed.

Next, as shown in FIG. 2, a recording layer was placed in an ID booklet that had a hot-melt layer (8), and was pressed onto the hot-melt layer for 10 seconds at approx. 120° C. As a result, an ID booklet illustrated in FIG. 1 was obtained, wherein the ID booklet not only had a clearly defined image but also character data, signal data 5 and color image data 4.

4. BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective side view of an ID booklet that includes an ID card of the invention;

FIG. 2 is a cross-section of showing an ID booklet portion, and an ID card portion which is later sealed with a plastic film lamination after image formation.

In the drawings, numeral 1 denotes an ID booklet; 2 denotes a booklet portion; 3 denotes an ID card portion; 4 denotes a color image data; 5 denotes character or signal data; 6 denotes an image recording layer; 7 denotes a plastic film; and 8 denotes a hot-melt layer.

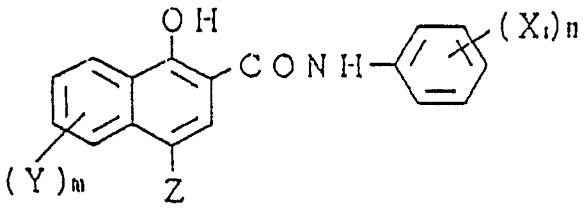
Claims

1. A heat developing color photosensitive material comprising a support having thereon a photosensitive silver halide, a reducing agent and a dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region from 400 nm to 700 nm, wherein said support further has thereon an infrared dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region longer than 725 nm.

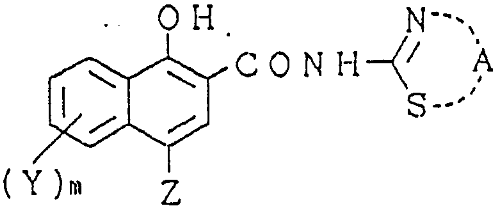
2. The heat developing color photosensitive material of claim 1, wherein said infrared dye providing substance is a compound capable of forming a dye by coupling.

3. The heat developing color photosensitive material of claim 1, wherein said infrared dye providing substance is a compound represented by Formula (1) or (2);

Formula (1)



Formula (2)



wherein X_1 represents an electron attracting group; n represents an integer of 1 to 3; when n is 2 or 3, two or three X_1's may be identical or different from each other; Y represents $COOR_1$, $SO_2NR_1R_2$, $CONR_1R_2$, NR_1R_2, NR_1COR_2, $NR_1SO_2R_2$, wherein R_1 and R_2 indepently represent a hydrogen atom, an alkyl group or an aryl group, or a halogen atom; m represents an integer of 0 to 4; when m is not less than 2, a plurality of Y may be identical or different from each other; Z represents a hydrogen atom or a group capable of being released by coupling; A represents a group of atoms needed for forming a 5-membered ring, wherein said ring may be that condensed with another ring.

4. The heat developing color photosensitive material of claim 1, wherein a molecular weight of said infrared dye providing substance is 700 or less.

5. The heat developing color photosensitive material of claim 1, wherein a molecular weight of said infrared dye providing substance is 500 or less.

6. The heat developing color photosensitive material of claim 1, wherein said infrared dye providing substance is a compound having a ballast group in the molecular structure.

7. The heat developing color photosensitive material of claim 1, wherein said Z represents a ballast group.

8. The heat developing color photosensitive material of claim 1, wherein said infrared dye providing substance is a compound represented by Formula (A);

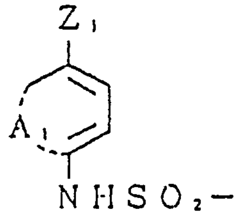
Formula (A)

$(Y - L)_q - X$

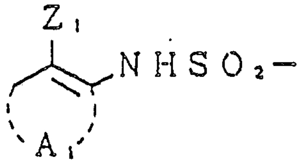
wherein X represents an infrared dye residue whose λ max is in the wavelength region longer than 725 nm; Y represents a group that has a property which varies diffusibility after developing different from that before developing; L represents a linkage group or a bivalent bonding group; q represents 1 or 2.

9. The heat developing color photosensitive material of claim 8, wherein said Y is a group represented by Formula (4), (5), (6), (7) or (8);

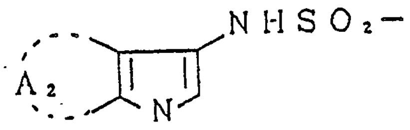
Formula (4)



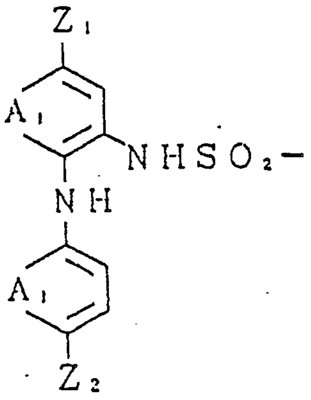
Formula (5)



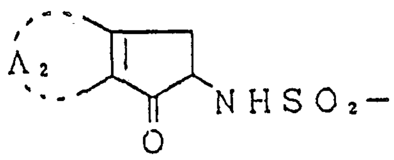
Formula (6)



Formula (7)



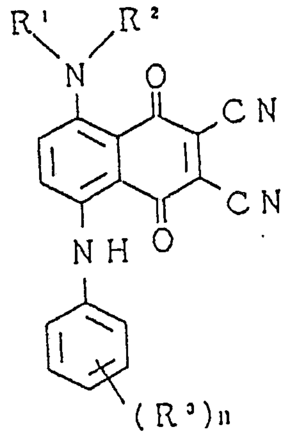
Formula (8)



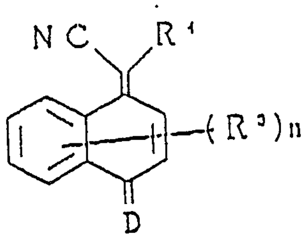
wherein A_1 represents an atomic group needed for forming a benzene ring or naphthalene ring; A_2 represents an atomic group needed for forming a condensed benzene ring; Z_1 and Z_2 independently represent a hydroxy group, an amino group or a group that is capable of providing a hydroxy group or an amino group.

10. The heat developing color photosensitive material of claim 8, wherein said X is a group represented by Formula (9), (10), (11) or (12);

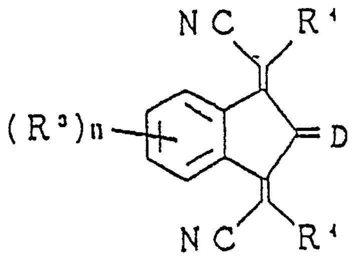
Formula (9)



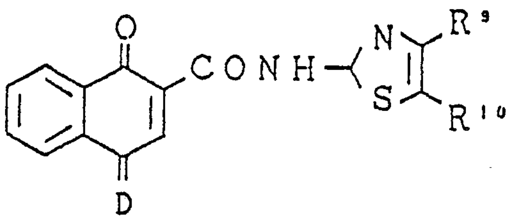
Formula (10)



Formula (11)

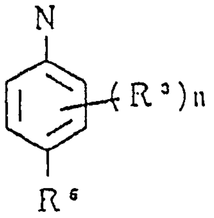


Formula (12)



wherein R^1 and R^2 independently represent a substituted or unsubstituted alkyl group having 1 to 4 carbon atoms or a hydrogen atom; R^3 represents a halogen atom, an alkyl group, an alkoxy group, an alkylamino group, an aralkyl group, a cycloalkyl group, an aryloxy group, an amino group, a sulfonylamino group, an acylamino group, an acyl group, a sulfonyl group, a carbamoyl group, a sulfamoyl group, a ureido group, an alkylthio group, an arylthio group, a hydroxy group, a cyano group or a carboxyl group; n represents an integer of 0 to 3; R^4 represents an electron attracting group; R^9 and R^{10} independently represent an alkyl group, an aralkyl group, an aryl group, an alkoxy group or a hydrogen group or R^8 and R^{10} are allowed to be bonded together to form a ring; D is represented by the following Formula E;

Formula E



wherein R^3 represents a halogen atom, an alkyl group, an alkoxy group, an alkylamino group, an aralkyl group, a cycloalkyl group, an aryloxy group, an amino group, a sulfonylamino group, an acylamino group, an acyl group, a sulfonyl group, a carbamoyl group, a sulfamoyl group, a ureido group, an alkylthio group, an arylthio group, a hydroxy group, a cyano group or a carboxyl group; n represents an integer of 0 to 3; R^6 represents a hydroxy group or NR^7R^8 wherein R^7 and R^8 independently represent a substituted or unsubstituted alkyl group or R^7 and R^8, R^7 and R^3 or R^8 and R^3 are allowed to be bonded together to form a ring;

11. The heat developing color photosensitive material of claim 1, wherein said infrared dye substance is incorporated into a layer having a cyan dye providing substance.

12. The heat developing color photosensitive material of claim 1, wherein an amount added of said infrared dye substance is 0.1g to 10g per square meter of said material.

13. A method of treating a heat developing color photosensitive material comprising a support having thereon a photosensitive silver halide, a reducing agent and a dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region from 400nm to 700nm, wherein said support further has thereon an infrared dye providing substance capable of forming or releasing a dye having maximum absorption in the wavelength region longer than 725 nm comprising the steps of:

(a) imagewise exposing said material,
(b) developing by heating said material,
(c) reading with light whose wavelength is in the wavelength region longer than 750 nm.

FIG.1

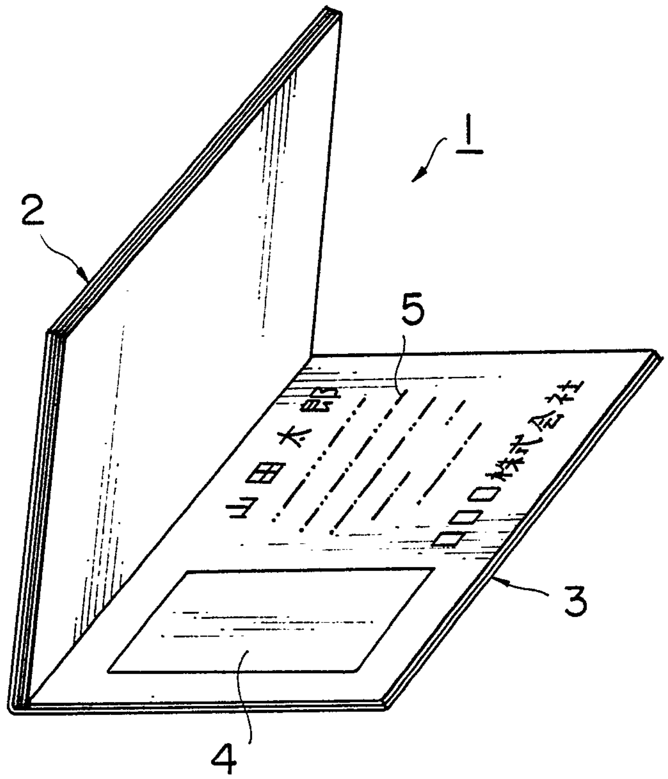


FIG.2